

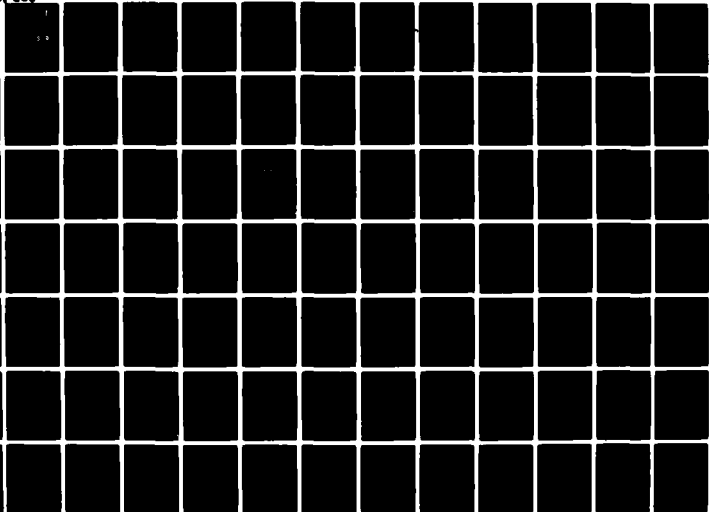
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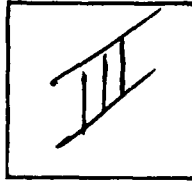
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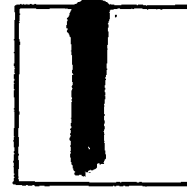
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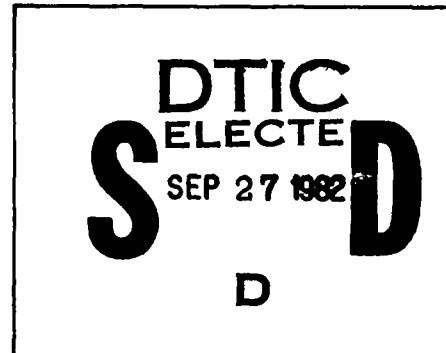
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**RESEARCH AND DEVELOPMENT OF METHODS FOR
ESTIMATING PHYSICOCHEMICAL PROPERTIES OF
ORGANIC COMPOUNDS OF ENVIRONMENTAL CONCERN**

**FINAL REPORT, PHASE II
(PART 2 OF 2 PARTS)**

by

Warren J. Lyman, Ph.D.*
James D. Birkett, Ph.D.
Sara E. Byshe
Cathy Campbell, Ph.D.
Clark F. Grain
John H. Hagopian
Judith C. Harris, Ph.D.

Michael J. Hayes
Leslie H. Nelken
Carl E. Rechsteiner, Jr., Ph.D.
William F. Reehl**
Kate M. Scow
Richard G. Thomas
William A. Tucker, Ph.D.

of Arthur D. Little, Inc.

and

David H. Rosenblatt, Ph.D.**
(Contracting Officer's Technical Representative)
US Army Medical Bioengineering Research and Development Laboratory

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*Contributor and editor. **Editor

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	(continued, over)									
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report contains selected, evaluated estimation methods for 26 environmentally important physicochemical properties of organic chemicals. The methods selected are applicable to a variety of chemical classes, are easy to use, require a minimum of input data, and are reasonably accurate. Each method has a descriptive text, step-by-step instructions, worked-out examples, and supplementary information allowing the user to estimate the likely uncertainty of an estimated value. Approximately 800 literature references cited.										

7. (cont.)

Contributors:

James D. Birkett, Ph.D.
Sara E. Bysshe
Cathy Campbell, Ph.D.
Clark F. Grain
John H. Hagopian
Judith C. Harris, Ph.D.
Michael J. Hayes

Warren J. Lyman, Ph.D.
Leslie H. Nelken
Carl E. Rechsteiner, Jr., Ph.D.
Kate M. Scow
Richard G. Thomas
William A. Tucker, Ph.D.

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octanol/water partition coefficient; solubility in water; solubility in various solvents; adsorption coefficient for soils and sediments; bioconcentration factor in aquatic organisms; acid dissociation constant; rate of hydrolysis; rate of aqueous photolysis; rate of biodegradation; atmospheric residence time; activity coefficient; boiling point; heat of vaporization; vapor pressure; volatilization from water; volatilization from soil; diffusion coefficients in air and water; flash points of pure substances; densities of vapors, liquids and solids; surface tension; interfacial tension with water; liquid viscosity; heat capacity; thermal conductivity; dipole moment; index of refraction; molar refractivity; critical temperature; critical pressure; Henry's law constant; mass transfer coefficients; molar volume; parachor; data sources; simple linear regression; propagation of errors; future research needs.

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**RESEARCH AND DEVELOPMENT OF METHODS FOR
ESTIMATING PHYSICOCHEMICAL PROPERTIES OF
ORGANIC COMPOUNDS OF ENVIRONMENTAL CONCERN**

**FINAL REPORT, PHASE II
(PART 2 OF 2 PARTS)**

by

Warren J. Lyman, Ph.D.*
James D. Birkett, Ph.D.
Sara E. Bysshe
Cathy Campbell, Ph.D.
Clark F. Grain
John H. Hagopian
Judith C. Harris, Ph.D.

Michael J. Hayes
Leslie H. Nelken
Carl E. Rechsteiner, Jr., Ph.D.
William F. Reehl**
Kate M. Scow
Richard G. Thomas
William A. Tucker, Ph.D.

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David H. Rosenblatt, Ph.D.**
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*Contributor and editor. **Editor

11

ACTIVITY COEFFICIENT

Clark F. Grain

11-1 INTRODUCTION

The purpose of this chapter is to provide methods of estimating the activity coefficients of components in solution. The discussion will be limited to binary systems although, in principle, the methods are applicable to multicomponent equilibria. The introductory remarks below may be supplemented by material in Refs. 8 and 21.

As applied to solutions, an activity coefficient, γ , is a correction factor compensating for non-ideal behavior. Consider, for example, an ideal binary solution of two organic liquids at a given temperature, where the number of moles of the first compound is n_1 and that of the second, n_2 . The mole fractions of the two are, respectively, $x_1 = n_1/(n_1 + n_2)$ and $x_2 = n_2/(n_1 + n_2)$. If the vapor pressures of the pure liquids are P_1° and P_2° , then, for any mixture, the partial pressure of component 1 is expressed as

$$P_1 = x_1 P_1^\circ \quad (11-1)$$

Similarly,

$$P_2 = x_2 P_2^\circ \quad (11-2)$$

If the two liquids form a non-ideal mixture, however, we should apply a variable correction factor, γ (the activity coefficient), so that

$$P_1 = \gamma_1 x_1 P_1^\circ \quad (11-3)$$

and

$$P_2 = \gamma_2 x_2 P_2^0 \quad (11-4)$$

We use the convention that $\gamma = 1$ for the pure components 1 and 2. In general, $\gamma > 1$ for dilute solutions of a given component in a given solvent. As the solution of this component becomes increasingly dilute, the value of γ asymptotically approaches a limiting value, γ^∞ . The product $\gamma_1 x_1$ is referred to as the activity, a_1 , and may be applied to properties other than vapor pressure.

Knowledge of the activity coefficients of the various components is useful in estimating quantities important to the environmental scientist. Examples of such quantities include solubility limits,¹ Henry's law constants, octanol-water partition coefficients² and solution equilibria in general. As an example, Lyman (see §1-5, Chapter 1) has shown that the octanol-water partition coefficient, K_{ow} , is proportional to the ratio of activity coefficients of a component A in water and octanol; thus,

$$K_{ow} = 0.151 \frac{(\gamma_w^A)^\infty}{(\gamma_o^A)^\infty} \quad (11-5)$$

where $(\gamma_w^A)^\infty, (\gamma_o^A)^\infty$ = infinite dilution activity coefficients of component A in water and octanol, respectively.³ For the process engineer a knowledge of activity coefficients is invaluable in calculations involving multi-component phase equilibria.

Activity coefficients are, of course, dimensionless and range in value from about 0.4 to upwards of 10^7 .

11-2 AVAILABLE METHODS

The fundamental equation that defines the activity coefficient for a binary system is⁴

1. Methods of estimating solubilities, using activity coefficients, are described in Chapter 3.
2. Methods of estimating K_{ow} , using activity coefficients, are described in Chapter 1.
3. A similar relationship is given by Mackay [13], except that the coefficient is given as 0.115 rather than 0.151.
4. Detailed discussion of the defining equations 11-1 through 11-8 are given in standard texts such as *Physical Chemistry* by N.K. Adam, Oxford University Press, London (1958) and in Refs. 8, 19, and 21.

$$\begin{aligned}
 G^M &= RT(n_1 \ln a_1 + n_2 \ln a_2) \\
 &= \underbrace{RT(n_1 \ln x_1 + n_2 \ln x_2)}_{G^I} + \underbrace{RT(n_1 \ln \gamma_1 + n_2 \ln \gamma_2)}_{G^E} \quad (11-6)
 \end{aligned}$$

where G^M is the energy of mixing, R is the gas constant, and T is the temperature. The two terms on the right side of this equation correspond to the Gibbs free energy of mixing for an ideal mixture (G^I) and the "excess" Gibbs free energy (G^E). From this expression for G^E , we obtain

$$\left(\frac{\partial G^E}{\partial n_1} \right) = RT \ln \gamma_1 \quad (11-7)$$

and

$$\left(\frac{\partial G^E}{\partial n_2} \right) = RT \ln \gamma_2 \quad (11-8)$$

Thus, in principle, we may relate activity coefficients to composition in mole fraction. All methods of accomplishing this are based upon assuming some analytical form for G^E subject to the conditions $G^E \propto n_1 + n_2$ at fixed composition and $G^E = 0$ when x_1 or $x_2 = 0$. The simplest expression satisfying these conditions is

$$G^E = (n_1 + n_2) A_1 x_1 x_2 \quad (11-9)$$

Using Eqs. 11-7 and 11-8 in Eq. 11-9, we obtain

$$\ln \gamma_1 = \frac{A_1}{RT} x_2^2 \quad (\approx x_2^2 \ln \gamma_1^\infty) \quad (11-10)$$

$$\ln \gamma_2 = \frac{A_1}{RT} x_1^2 \quad (\approx x_1^2 \ln \gamma_2^\infty) \quad (11-11)$$

(The equivalency of A_1/RT to $\ln \gamma_1^\infty$ follows from the fact that $x_2 \approx 1$ when the concentration of component 1 approaches zero; the same applies to $\ln \gamma_2^\infty$.)

The parameter A_1 can be evaluated from binary vapor-liquid data or it may be approximated as $RT \ln \gamma_1^\infty$. Although Eq. 11-9 is presented as an example, it has little practical value. It contains only one adjustable parameter and hence is restricted to those systems in which $\gamma_1^\infty \approx \gamma_2^\infty$.

Equation 11-9 is called the two-suffix Margules equation and is essentially empirical. One failing of this equation is that S^E , the excess entropy of mixing, is not taken into account. Similar equations with the same deficiency are listed in Table 11-1 under the heading of enthalpic equations.

The equations listed can be used with some success in estimating solubility limits, particularly for systems with low solubilities, as described in Chapter 3. Furthermore, the van Laar equation has been used to represent vapor-liquid equilibria with reasonable accuracy [15,19]. However, when used to predict liquid-liquid equilibria, such enthalpic equations are unsatisfactory [15]. Another failing of these equations is that when the adjustable parameters are evaluated using binary data obtained at intermediate compositions, extrapolation to the dilute regions is unsatisfactory. Finally, the enthalpic relations all too often predict immiscibility when, in fact, it does not exist.

In 1964 Wilson [27] introduced the concept of local composition which, in effect, takes into account S^E . Wilson used local volume fractions in his final equation. Subsequent investigations by Orye [16], Renon [20], and Abrams [1] have shown that the local composition concept is a powerful tool in representing and predicting equilibrium behavior in both vapor-liquid and liquid-liquid systems.

The equations that have been derived from the local-composition concept have commonly been termed entropic equations. These are also listed in Table 11-1. The Wilson equation cannot predict immiscibility; i.e., no values of the parameters in this equation allow for the prediction of a miscibility gap.

Recent advances [5,6,9] have led to group contribution techniques in which the solute and solvent molecules are divided into groups such as OH, CH₂, and NH₂. Group parameters are then evaluated through use of experimental data. Once the group parameters have been evaluated they may be used to predict the behavior of other systems containing those groups, but for which there are no experimental data. These group contribution schemes have been successfully applied in the Wilson equation [5] and the UNIQUAC (Universal Quasi Chemical) equation [9].

TABLE 11-1

Some Models for the Excess Gibbs Energy and Subsequent Activity Coefficients for Binary Systems

Name	$g^E = G^E / (n_1 + n_2)$	Binary Parameters	$\ln \gamma_1$ and $\ln \gamma_2$
Enthalpic Equations			
Two-suffix ^a Margules	$g^E = A x_1 x_2$	A	$RT \ln \gamma_1 = A x_2^2$ $RT \ln \gamma_2 = A x_1^2$
Three-suffix ^a Margules	$g^E = x_1 x_2 [A + B (x_1 - x_2)]$	A, B	$RT \ln \gamma_1 = (A + 3B) x_2^2 - 4B x_2^3$ $RT \ln \gamma_2 = (A - 3B) x_1^2 + 4B x_1^3$
van Laar	$g^E = \frac{A x_1 x_2}{x_1 (A/B) + x_2}$	A, B	$RT \ln \gamma_1 = A \left(1 + \frac{A}{B} \frac{x_1}{x_2} \right)^{-2}$ $RT \ln \gamma_2 = B \left(1 + \frac{B}{A} \frac{x_2}{x_1} \right)^{-2}$
Four-suffix ^a Margules	$g^E = x_1 x_2 [A + B (x_1 - x_2) + C (x_1 - x_2)^2]$	A, B, C	$RT \ln \gamma_1 = (A + 3B + 5C) x_2^2 - 4(B + 4C) x_2^3 + 12C x_2^4$ $RT \ln \gamma_2 = (A - 3B + 5C) x_1^2 + 4(B - 4C) x_1^3 + 12C x_1^4$
Entropic Equations			
Wilson	$\frac{g^E}{RT} = -x_1 \ln (x_1 + \Lambda_{12} x_2) - x_2 \ln (x_2 + \Lambda_{21} x_1)$	$\Lambda_{12}, \Lambda_{21}$	$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12} x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right)$ $\ln \gamma_2 = -\ln (x_2 + \Lambda_{21} x_1) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right)$
NRTL ^b	$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right)$ where $\tau_{12} = \frac{\Delta g_{12}}{RT}$ $\tau_{21} = \frac{\Delta g_{21}}{RT}$ $\ln G_{12} = -\alpha_{12} \tau_{12}$ $\ln G_{21} = -\alpha_{12} \tau_{21}$		$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right]$ $\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]$

(Continued)

TABLE 11-1 (Continued)

Name	$g^E = G^E / (n_1 + n_2)$	Binary Parameters	$\ln \gamma_1$ and $\ln \gamma_2$
Entropic Equations (continued)			
UNIQUAC^d			
	$g^E = g^E \text{ (combinatorial)} + g^E \text{ (residual)}$ $\frac{g^E \text{ (combinatorial)}}{RT} = x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2}$ $+ \frac{z}{2} \left(q_1 x_1 \ln \frac{\theta_1}{\Phi_1} + q_2 x_2 \ln \frac{\theta_2}{\Phi_2} \right)$ $\frac{g^E \text{ (residual)}}{RT} = -q_1 x_1 \ln [\theta_1 + \theta_2 \tau_{21}] - q_2 x_2 \ln [\theta_2 + \theta_1 \tau_{12}]$ $\Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \quad \theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}$ $\ln \tau_{21} = -\frac{\Delta u_{21}}{RT} \quad \ln \tau_{12} = -\frac{\Delta u_{12}}{RT}$ <p>r and q are pure-component parameters and coordination number $z = 10$.</p>	Δu_{12} and Δu_{21} ^c	$\ln \gamma_1 = \ln \frac{\Phi_1}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\Phi_1} + \Phi_2 \left(\frac{\theta_1}{\theta_1 + \theta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_1 + \theta_2 \tau_{12}} \right)$ $- q_1 \ln (\theta_1 + \theta_2 \tau_{21}) + \theta_2 q_1 \left(\frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_1 + \theta_2 \tau_{12}} \right)$ <p>where $i = 1, j = 2$ or $i = 2, j = 1$</p> $\ell_i = \frac{z}{2} (r_i - q_i) - (r_i - 1)$ $\ell_j = \frac{z}{2} (r_j - q_j) - (r_j - 1)$

a. Two-suffix signifies that the expansion for g^E is quadratic in mole fraction. Three-suffix signifies a third-order, and four-suffix signifies a fourth-order equation.

b. NRTL = Non Random Two Liquid.

c. $\Delta g_{12} = g_{12} - g_{22}$; $\Delta g_{21} = g_{21} - g_{11}$.

d. UNIQUAC = Universal Quasi Chemical.

e. $\Delta u_{12} = u_{12} - u_{22}$; $\Delta u_{21} = u_{21} - u_{11}$.

Source: Reid, Prausnitz and Sherwood [21].

In what follows we will concentrate on two methods of estimating activity coefficients. The first of these will involve the estimation of γ^∞ , the infinite dilution activity coefficient. The method to be used was introduced by Pierotti *et al.* [18] and will be described in detail in §11-4.

The infinite dilution activity coefficient alone can be used to estimate solubility limits (Chapter 3), octanol-water partition coefficients (Chapter 1), and Henry's law constants.⁵ It may also be used to estimate the parameters in any two-parameter equation, e.g., the van Laar equation, which will then allow us to estimate the activity coefficient at any composition.

The second method, which estimates the concentration dependence of γ_i directly, uses the UNIQUAC equation combined with group contribution techniques. It has been called the UNIFAC (UNIQUAC Functional Group Activity Coefficients) method [15]. Other group contribution schemes such as ASOG (Analytical Solution of Groups) [13] have been used successfully. However, we chose the UNIFAC method because of its stronger theoretical base. Table 11-2 gives an overview of the methods chosen.

11-3 METHOD ERRORS

Large percentage errors can be tolerated in estimates of activity coefficients, particularly with respect to γ^∞ . It has been found [21], for example, that a $\pm 10\%$ variation in γ^∞ does not affect predictions of vapor-liquid equilibria. Furthermore, errors as high as $\pm 50\%$ in γ^∞ often do not affect γ in the high concentration range by more than $\pm 10\%$. Generally speaking, the correlations discussed in this chapter are capable of predicting γ^∞ to within $\pm 25\%$ of the true value. For example, for Method 1, Pierotti *et al.* [18] gave an overall average deviation of 8% in γ^∞ , although in isolated instances errors as high as 350% were obtained.

For the UNIFAC method (Method 2) Table 11-3 lists results obtained for a number of systems with water. The average error in γ is 23.5% and the maximum error is 90%.

5. Henry's Law constant (H) \approx (vapor pressure)/(solubility). Thus the vapor pressure must also be known to calculate H . (See Example 11-2.)

TABLE 11-2

Characteristics of Methods 1 and 2

Method	Gives	Input Required	Ease of Calculation	Method Error	Limitations
Method 1 Pierotti <i>et al.</i> [18] (§ 11-4)	γ^∞ for $25^\circ\text{C} \leq T \leq 100^\circ\text{C}$ (See Note a)	Chemical structure	Easy	Avg. 8% Max. 350% ^b	Limited to certain solute and solvent classes. See Table 11-4.
Method 2 UNIFAC [9] (§ 11-5)	γ at any solute concentration and temperature	Chemical structure	Difficult	Avg. 23.5% Max. 95% ^c	Limited to chemicals with common structures and functional groups. See Tables 11-6 and -7.

a. Although Method 1 yields only γ^∞ , equations are provided in § 11-4 to allow estimation of γ at any solute concentration once γ^∞ has been found.

b. Based on information in Ref. 18.

c. Based on information in Ref. 9. See Table 11-3 for details.

TABLE 11-3

Comparison of Experimental and Calculated Activity Coefficients
(Method 2)

System	T (K)	X_1^a	γ (exp.)	γ (calc.)
Hydrocarbons				
(These activity coefficients are based on liquid-liquid equilibria)				
Water-Hexane	293.2	0.000	1,880	2,040
Hexane-Water	298.2	0.000	489,000	402,000
Water-Benzene	313.2	0.000	226.3	308.2
Benzene-Water	333.2	0.000	1,730	1,670
Water-Toluene	333.2	0.000	3,320	391
Toluene-Water	333.2	0.000	3,390	7,820
Oxygenated Hydrocarbons				
Water-Ethanol	313.2	0.000	4.748	3.184
Ethanol-Water	313.2	0.043	2.398	2.210
Water-1-Propanol	363.2	0.117	2.845	3.079
1-Propanol-Water	363.2	0.111	4.594	5.066
Water-2-Propanol	328.2	0.141	2.965	2.993
2-Propanol-Water	328.2	0.046	7.706	10.572
Water-1-Butanol	333.2	0.050	4.237	4.339
1-Butanol-Water	333.2	0.016	38.61	54.66
Water-Methanol	340.2	0.154	1.505	1.543
Methanol-Water	368.2	0.029	2.097	2.126
Water-Phenol	348.2	0.321	1.842	2.185
Phenol-Water	348.2	0.015	20.43	23.42
Water-Acetic acid	388.6	0.050	1.769	1.697
Acetic acid-Water	373.7	0.100	2.027	2.300
Water-Propanoic acid	394.3	0.115	2.382	2.125
Propanoic acid-Water	373.1	0.108	3.462	3.809
Water-Acetaldehyde	293.2	0.100	2.982	2.688
Acetaldehyde-Water	293.2	0.100	2.653	2.606
Water-Methyl acetate	308.2	0.019	21.25	20.17
Methyl acetate-Water	298.2	0.005	21.84	24.94

(Continued)

TABLE 11-3 (Continued)

System	T (K)	X ₁ ^a	γ(exp.)	γ(calc.)
Oxygenated Hydrocarbons (cont'd.)				
Water-Ethyl acetate	343.2	0.032	8.025	8.378
Ethyl acetate-Water	343.2	0.000	21.97	14.71
Water-Acetone	333.2	0.263	2.551	2.362
Acetone-Water	333.2	0.072	5.638	6.736
Water-Tetrahydrofuran	323.2	0.078	6.800	5.690
Tetrahydrofuran-Water	323.2	0.075	10.12	14.67
Water-1,4-Dioxane	365.9	0.120	2.430	3.400
1,4-Dioxane-Water	365.1	0.073	4.670	9.840
Nitrogen Compounds				
Water-Aniline	433.2	0.011	4.985	4.277
Aniline-Water	371.8	0.021	34.16	50.65
Water-Butylamine	350.2	0.045	1.720	1.587
Butylamine-Water	361.3	0.020	12.58	12.95
Water-Diethylamine	311.5	0.100	3.074	1.665
Diethylamine-Water	311.5	0.100	2.485	3.398
Water-Acetonitrile	303.2	0.080	6.778	6.041
Acetonitrile-Water	303.2	0.070	9.666	8.201

a. Mole fraction of the solute (i.e., the first chemical listed for each system). Note that when $x_1 = 0$, $\gamma = \gamma^\infty$.

Source: Fredenslund, Gmehling and Rasmussen [8].

11-4 METHOD 1 — INFINITE DILUTION ACTIVITY COEFFICIENTS

This method requires a knowledge of the molecular structure. As introduced by Pierotti *et al.* [18], the technique relates γ^∞ to the molecular structures of the solute and solvent molecules through an equation that contains the number of carbon atoms for both species. Thus, in general,

$$\log \gamma_1^\infty = A_{1,2} + B_2 \frac{N_1}{N_2} + \frac{C_1}{N_1} + D (N_1 - N_2)^2 + \frac{F_2}{N_2} \quad (11-12)$$

where subscript 1 refers to solute and 2 to solvent and

$A_{1,2}$ = coefficient which depends on nature of solute and solvent functional groups

- B_s = coefficient which depends only on nature of solvent functional group
 C_1 = coefficient which depends only on solute functional group
 D = coefficient independent of solute and solvent functional groups
 F_s = coefficient which essentially depends only on nature of solvent functional group
 N_1, N_s = number of carbon atoms in solute and solvent, respectively

For secondary and tertiary alcohols the C_1 term is modified such that it becomes $C_1 (1/N_1' + 1/N_1'')$ for secondary alcohols and $C_1 (1/N_1' + 1/N_1'' + 1/N_1''')$ for tertiary alcohols, where the primed N 's are carbon numbers of the respective branches counted from the polar groupings. Thus, for *tert*-butyl alcohol, the central carbon is counted in each branch, i.e., $N_1' = N_1'' = N_1''' = 2$ even though the total carbon number is four. If the alcohol is the solvent, a similar argument holds for the F_s term.

Alternatively, one may consider all alcohols as a single homologous series by using terms such as $C_1(1/N_1 - 1)$, $C_1[(1/N_1' - 1) + (1/N_1'' - 1)]$ and $C_1[(1/N_1' - 1) + (1/N_1'' - 1) + (1/N_1''' - 1)]$ for primary, secondary and tertiary alcohols, respectively. Thus, a single value of C_1 covers all alcohols with little loss in accuracy. The F_s term may be represented similarly if the alcohol is the solvent. Other modifications are needed for ketones, acetals, and cyclic hydrocarbons. Table 11-4, which is taken from Ref. 18, footnotes the necessary modifications and gives values of the coefficients in Eq. 11-12. Three additional systems (paraffins- n alcohols, water-paraffins, and water-alkyl benzenes), determined by this writer, are included in the table.

The Pierotti correlations were later extended by Tsonopoulos and Prausnitz [25] to include the effect of substituents on alkyl benzenes in dilute aqueous solutions. A detailed analysis of $\log \gamma^\infty$ data resulted in a number of correction factors to be added to calculated values of $\log \gamma^\infty$. Their table is reproduced here as Table 11-5, supplemented by correction factors for condensed-ring derivatives, biphenyl derivatives, and polymethyl substituents. The authors derived separate equations for each of the above-named groups. However, we have found that the single equation for alkylbenzenes in water, with the correction factors listed, is adequate.

TABLE 11-4

**Correlating Constants for Activity Coefficients at Infinite Dilution,
Homologous Series of Solutes and Solvents**

Solute (1)	Solvent (2)	Temp. (°C)	A _{1,2}	B ₂	C ₁	D	F ₂	See Note
<i>n</i> -Acids	Water	25	-1.00	0.622	0.490	0	0	a
		50	-0.80	0.590	0.290	0	0	a
		100	-0.620	0.517	0.140	0	0	a
<i>n</i> -Primary alcohols	Water	25	-0.995	0.622	0.558	0	0	a
		60	-0.755	0.583	0.460	0	0	a
		100	-0.420	0.517	0.230	0	0	a
Secondary alcohols	Water	25	-1.220	0.622	0.170	0	0	b
		60	-1.023	0.583	0.252	0	0	b
		100	-0.870	0.517	0.400	0	0	b
Tertiary alcohols	Water	25	-1.740	0.622	0.170	0	0	c
		60	-1.477	0.583	0.252	0	0	c
		100	-1.291	0.517	0.400	0	0	c
Alcohols, general	Water	25	-0.525	0.622	0.475	0	0	d
		60	-0.33	0.583	0.39	0	0	d
		100	-0.15	0.517	0.34	0	0	d
<i>n</i> -Allyl alcohols	Water	25	-1.180	0.622	0.558	0	0	a
		60	-0.929	0.583	0.460	0	0	a
		100	-0.650	0.517	0.230	0	0	a
<i>n</i> -Aldehydes	Water	25	-0.780	0.622	0.320	0	0	a
		60	-0.400	0.583	0.210	0	0	a
		100	-0.3	0.517	0	0	0	a
<i>n</i> -Alkene aldehydes	Water	25	-0.720	0.622	0.320	0	0	a
		60	-0.540	0.583	0.210	0	0	a
		100	-0.298	0.517	0	0	0	a
<i>n</i> -Ketones	Water	25	-1.475	0.622	0.500	0	0	b
		60	-1.040	0.583	0.330	0	0	b
		100	-0.621	0.517	0.200	0	0	b
<i>n</i> -Acetals	Water	25	-2.556	0.622	0.486	0	0	e
		60	-2.184	0.583	0.451	0	0	e
		100	-1.780	0.517	0.426	0	0	e
<i>n</i> -Ethers	Water	20	-0.770	0.640	0.195	0	0	b
<i>n</i> -Nitriles	Water	25	-0.587	0.622	0.760	0	0	a
		60	-0.368	0.583	0.413	0	0	a
		100	-0.095	0.517	0	0	0	a
<i>n</i> -Alkene nitriles	Water	25	-0.520	0.622	0.760	0	0	a
		60	-0.323	0.583	0.413	0	0	a
		100	-0.074	0.517	0	0	0	a

(Continued)

TABLE 11-4 (Continued)

Solute (1)	Solvent (2)	Temp. (°C)	A _{1,2}	B ₂	C ₁	D	F ₂	See Note
<i>n</i> -Esters	Water	20	-0.930	0.640	0.260	0	0	b
<i>n</i> -Formates	Water	20	-0.585	0.640	0.260	0	0	a
<i>n</i> -Monoalkyl chlorides	Water	20	1.265	0.640	0.073	0	0	a
<i>n</i> -Paraffins	Water	16	0.688	0.642	0	0	0	a
<i>n</i> -Alkylbenzenes	Water	25	3.554	0.622	-0.466	0	0	f
Alcohols, general	Paraffins	25	1.960	0	0.475	-0.00049	0	d
		60	1.460	0	0.390	-0.00057	0	d
		100	1.070	0	0.340	-0.00061	0	d
<i>n</i> -Ketones	Paraffins	25	0.0877	0	0.757	-0.00049	0	b
		60	0.016	0	0.680	-0.00057	0	b
		100	-0.067	0	0.605	-0.00061	0	b
Water	<i>n</i> -Alcohols	25	0.760	0	0	0	-0.630	a
		60	0.680	0	0	0	-0.440	a
		100	0.617	0	0	0	-0.280	a
Water	<i>sec</i> -Alcohols	80	1.208	0	0	0	-0.690	c
Water	<i>n</i> -Ketones	25	1.857	0	0	0	-1.019	c
		60	1.493	0	0	0	-0.73	c
		100	1.231	0	0	0	-0.557	c
Ketones	<i>n</i> -Alcohols	25	-0.088	0.176	0.50	-0.00049	-0.630	g
		60	-0.035	0.138	0.33	-0.00057	-0.440	g
		100	-0.035	0.112	0.20	-0.00061	-0.280	g
Acetals	<i>n</i> -Alcohols	25	-0.701	0.176	0.320	-0.00049	-0.630	
		60	-0.239	0.138	0.210	-0.00057	-0.440	
Esters	<i>n</i> -Alcohols	25	0.212	0.176	0.260	-0.00049	-0.630	g
		60	0.055	0.138	0.240	-0.00057	-0.440	g
		100	0	0.112	0.220	-0.00061	-0.280	g
Acetals	<i>n</i> -Alcohols	60	-1.10	0.138	0.451	-0.00057	-0.440	h
Paraffins	Ketones	25	0	0.1821	0	-0.00049	0.402	i
		60	0	0.1145	0	-0.00057	0.402	i
		90	0	0.0746	0	-0.00061	0.402	i
Paraffins ¹	<i>n</i> -Alcohols	25	0.87	0.176	0	-0.00049	-0.630	
		60	0.80	0.138	0	-0.00057	-0.440	
		100	0.72	0.112	0	-0.00061	-0.280	
Water ¹	Paraffins	25	2.55	0	0	0	3.88	
Water ¹	<i>n</i> -Alkylbenzenes	25	3.04	0	0	0	-3.14	

(Continued)

TABLE 11-4 (Continued)

Modification of terms in Eq. 11-12:

- a. $B_2 N_1$
- b. $B_2 N_1, C_1 \left(\frac{1}{N'_1} + \frac{1}{N''_1} \right)$
- c. $B_2 N_1, C_1 \left(\frac{1}{N'_1} + \frac{1}{N''_1} + \frac{1}{N'''_1} \right), F_2 \left(\frac{1}{N'_2} + \frac{1}{N''_2} \right)$
- d. $B_2 N_1, C_1 \left(\frac{1}{N'_1} + \frac{1}{N''_1} + \frac{1}{N'''_1} - 3 \right)$
- e. $B_2 N_1, C_1 \left(\frac{1}{N'_1} + \frac{1}{N''_1} + \frac{2}{N'''_1} \right); N_1''' \text{ relates to } R''' \text{ in } R'(R'')C(OR)_2$
- f. $B_2 (N_1 - 6), C_1 \left(\frac{1}{N_1 - 4} \right)$
- g. $C_1 \left(\frac{1}{N'_1} + \frac{1}{N''_1} \right)$
- h. $C_1 \left(\frac{1}{N'_1} + \frac{1}{N''_1} + \frac{2}{N'''_1} \right); N_1''' \text{ relates to } R''' \text{ in } R'(R'')C(OR)_2$
- i. $F_2 \left(\frac{1}{N'_2} + \frac{1}{N''_2} \right)$

N_1, N_2 = total number of carbon atoms in molecules 1 and 2, respectively.

N', N'', N''' = number of carbon atoms in respective branches of branched compounds, counting the polar grouping; thus, for *t*-butanol, $N' = N'' = N''' = 2$.

j. Entries contributed by the author of this chapter.

Source: Pierotti, Deal and Derr [18] as modified by Reid, Prausnitz and Sherwood [21] and this author (see note j).

Some examples illustrating the estimation of γ^∞ for a variety of materials should be helpful at this point. The basic steps are as follows:

Basic Steps

- (1) Draw the structures of the chemical involved.
- (2) Use Table 11-4 to obtain the appropriate correlation constants and any modification of terms required.
- (3) Substitute the constants and modifications into Eq. 11-12 and calculate $\log \gamma^\infty$.
- (4) If the solute is an aromatic compound and water is the solvent, calculate $\log \gamma^\infty$ for the unsubstituted hydrocarbon; then use Table 11-5, as appropriate, to obtain corrections to $\log \gamma^\infty$.
- (5) The antilog of $\log \gamma^\infty$ (corrected, if appropriate) yields γ^∞ .

TABLE 11-5

Correction Factors for $\log \gamma_1^\infty$, per Group^a

Group	Δ	Group	Δ
F	0.14	NH ₂	-1.35
Cl	0.70	NO ₂	
Br	0.92	(hydrocarbons)	0.15
I	1.40	(<i>m</i> -, <i>p</i> -phenols)	0.30
OH		(<i>m</i> -, <i>p</i> -anilines)	1.00
(alcohols)	-1.90	CH ₃ (N ₁ ≥ 8)	-0.25
(phenols)	-1.70	C=C (in side chain)	-0.30
COOH		C≡C (in side chain)	-0.46
(in side chain)	-1.70	Polycyclic hydrocarbons	-1.11 per addi-
(on ring)	-0.70	(naphthenes and biphenyls)	tional ring

^a. Groups are attached to ring unless otherwise specified.

Source: Tsionopoulos and Prausnitz [25].

Example 11-1 Estimate the infinite-dilution activity coefficients in the system ethanol(1)-n-hexane(2) at 70°C [25].

- (1) The structure of ethanol is CH₃CH₂OH; for hexane the structure is CH₃(CH₂)₄CH₃. Thus N₁ = 2, N₂ = 6.
- (2) From Table 11-4 the correlation coefficients for alcohols in paraffin solvents at 25°C, 60°C and 100°C are given. The changes in all the coefficients except A_{1,2} are small enough such that the value at 60°C can be used without loss of accuracy. For A_{1,2} interpolation between 60°C and 100°C should be used for highest accuracy. Thus A_{1,2} (interpolated) = 1.40, B₂ = 0, C₁ = 0.390 and D = -0.00057. Under modification (d) the equation for $\log \gamma_1^\infty$ is

$$\log \gamma_1^\infty = A_{1,2} + B_2 N_1 + C_1 (1/N_1 - 1) + D (N_1 - N_2)^2$$

- (3) $\log \gamma_1^\infty = 1.400 + 0 + 0.39 (1/2 - 1) - 0.00057 (2 - 6)^2$
 $= 1.400 - 0.195 - 0.00912$
 $= 1.196$

- (4) $\gamma_1^\infty = \text{antilog}(1.196) = 15.7$. The experimental value is 18.1 [21] for an error of -13.3%.

For γ_2^∞ the indices are interchanged; i.e., we are now interested in the system hexane(1)-ethanol(2) with N₁ = 6 and N₂ = 2.

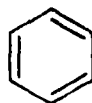
- (5) Repeating Step 2 from Table 11-4, for the paraffin-alcohol correlation, we note that the changes in all of the coefficients with respect to temperature are small enough such that the values at 60°C can be used with sufficient accuracy. Thus $A_{1,2} = 0.80$, $B_2 = 0.138$, $D = -0.00057$ and $F_2 = -0.440$. Equation 11-12 is used as is, with $C_1 = 0$; thus,

$$\begin{aligned} (6) \quad \log \gamma_2^\infty &= 0.80 + 0.138 (6/2) - 0.00057 (6-2)^2 - 0.440/2 \\ &= 0.80 + 0.414 - 0.00912 - 0.220 \\ &= 0.985 \end{aligned}$$

- (7) $\gamma_2^\infty = \text{antilog}(0.985) = 9.66$. The experimental value is 9.05 [22] for an error of +6.7%.

Example 11-2 Estimate the infinite dilution activity coefficients for the system benzene-water at 25°C. From these values estimate the solubility of benzene in water and water in benzene and Henry's law constant for benzene in water at 25°C.

- (1) Structure of benzene



$N_1 = 6$. For water $N_2 = 0$. However, this does not lead to an infinite B_2 term because footnote f of Table 11-4 dictates the use of a modified B_2 term.

- (2) From Table 11-4 the correlation coefficients for alkylbenzenes in water are $A_{1,2} = 3.554$, $B_2 = 0.622$ and $C_1 = -0.466$. There are no D and F_2 terms. Under modification (f) the equation for $\log \gamma_1^\infty$ is

$$\log \gamma_1^\infty = A_{1,2} + B_2 (N_1 - 6) + C_1 [1/(N_1 - 4)]$$

$$\begin{aligned} (3) \quad \log \gamma_1^\infty &= 3.554 + 0.622 (6 - 6) - 0.466 [1/(6 - 4)] \\ &= 3.321 \end{aligned}$$

- (4) $\gamma_1^\infty = \text{antilog}(3.321) = 2,094$. The experimental value is 2400 [4] for an error of -12.8%.

- (5) Repeating Step 2 with water as solute and benzene as solvent the correlation coefficients are $A_{1,2} = 3.04$ and $F_2 = -3.14$. Equation 11-12 is used as is, with $B_2 = C_1 = D = 0$.

$$\begin{aligned} (6) \quad \log \gamma_2^\infty &= 3.04 - \frac{3.14}{6} \\ &= 2.517 \end{aligned}$$

- (7) $\gamma_2^\infty = \text{antilog}(2.517) = 329$. The experimental value is 430 [9] for an error of -23.5%.
- (8) The methods of Chapter 3 allow us now to estimate the mutual solubilities in the benzene-water system. For benzene in water the solubility is inversely proportional to γ_1^∞ as $\gamma_1^\infty > 1000$; hence $x_1 = 1/\gamma_1^\infty \approx 4.8 \times 10^{-4}$ mole fraction. The experimental value is 4.2×10^{-4} [7]. For water in benzene γ_2^∞ is < 1000 but > 50 ; hence, Figure 3-5 of Chapter 3 is applicable, and $x_2 = 3.5 \times 10^{-3}$ mole fraction. The experimental value is 3.1×10^{-3} [7].
- (9) The Henry's law constant is defined as $H \approx P_{vp1}/S$ where P_{vp1} (atm) is the vapor pressure of pure component 1 at the system temperature (25°C) and S is the solubility in moles/m³. The vapor pressure of benzene at 25°C is estimated (Method 2, Chapter 14) as 95.5 mm or 0.126 atm. The estimated solubility S in moles/m³ of water is $S \approx 4.8 \times 10^{-4} \times 55.5 \times 10^3 = 26.6$ moles/m³. Thus $H = 0.126/26.6 = 4.7 \times 10^{-3}$ atm·m³/mol. The experimental value is 5.5×10^{-3} atm·m³/mole [26].

The estimated infinite-dilution activity coefficients can be used to determine the parameters in any two-parameter equation. For example, the parameters in the van Laar equation (Table 11-1) are given by $A = RT \ln \gamma_1^\infty$ and $B = RT \ln \gamma_2^\infty$; hence, at any value of x_1 and x_2 , the activity coefficients are given by

$$\ln \gamma_1 = \ln \gamma_1^\infty \left(1 + \frac{x_1 \ln \gamma_1^\infty}{x_2 \ln \gamma_2^\infty} \right)^{-2} \quad (11-13)$$

and

$$\ln \gamma_2 = \ln \gamma_2^\infty \left(1 + \frac{x_2 \ln \gamma_2^\infty}{x_1 \ln \gamma_1^\infty} \right)^{-2} \quad (11-14)$$

In the next example the activity coefficients at $x_1 = 0.292$ will be estimated.

Example 11-3 Estimate the infinite-dilution activity coefficients for the system n-pentane(1)-acetone(2) at their respective boiling points, $T_b \approx 309\text{K}$ (36°C) for pentane and 330K (57°C) for acetone. Use the infinite-dilution activity coefficients to estimate the activity coefficients at a composition of 0.292 mole fraction of n-pentane.

- (1) The structure of n-pentane is $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$. For acetone the structure is $(\text{CH}_3)_2\text{C}=\text{O}$.
- (2) From Table 11-4, there are no $A_{1,2}$ or C_1 terms for Eq. 11-12. The remaining correlation coefficients for paraffins in ketone solvents were interpolated (for

values at 36°C) and are: $B_2 = 0.1608$, $D = -0.00051$ and $F_2 = 0.402$. Under modification (i) the F_2 term is $F_2 (1/N'_2 + 1/N''_2)$ where the N_2 's refer to the number of carbons on either side of the carbonyl group plus the carbonyl carbon. Thus $N'_2 = N''_2 = 2$.

- (3) Substituting in Eq. 11-12

$$\begin{aligned}\log \gamma_1^\infty &= 0.1608 (5/3) - 0.00051 (5-3)^2 + 0.402 (1/2 + 1/2) \\ &= 0.668\end{aligned}$$

- (4) $\gamma_1^\infty = \text{antilog} (0.668) = 4.66$

- (5) Repeating Step 2 for acetone in pentane (using the coefficient values for 60°C) the correlation coefficients are $A_{1,2} = 0.016$, $B_2 = 0$, $C_1 = 0.680$, $D = -0.00057$ and there is no F_2 term. (Interpolation is unnecessary as the boiling point of acetone, 57°C, is close enough to the values given at 60°C.) Under modification (b) the C_1 term is changed to $C_1 (1/N'_1 + 1/N''_1)$ where the N_1 's have the same meaning given above when acetone was the solvent.

- (6) Substituting in Eq. 11-12

$$\begin{aligned}\log \gamma_2^\infty &= 0.016 + 0.680 (1/2 + 1/2) - 0.00057 (3-5)^2 \\ &= 0.694\end{aligned}$$

- (7) $\gamma_2^\infty = \text{antilog} (0.694) = 4.94$

- (8) To estimate γ_1 at $x_1 = 0.292$ we use Eq. 11-13 with $x_2 = 1 - x_1 = 0.708$

$$\begin{aligned}\ln \gamma_1 &= \ln (4.66) \left(1 + \frac{0.292 \ln (4.66)}{0.708 \ln (4.94)} \right)^{-2} \\ &= 1.539 \left(1 + \frac{0.292 \times 1.539}{0.708 \times 1.597} \right)^{-2} = 1.539 (1.397)^{-2} \\ &= 0.788 \\ \gamma_1 &= 2.20\end{aligned}$$

The experimental value is 2.22 [12] for an error of -0.9%.

- (9) To estimate γ_2 at $x_1 = 0.292$ Eq. 11-14 is used.

$$\begin{aligned}\ln \gamma_2 &= \ln (4.94) \left(1 + \frac{0.708 \ln (4.94)}{0.292 \ln (4.66)} \right)^{-2} \\ &= 1.597 (3.516)^{-2} \\ &= 0.129 \\ \gamma_2 &= 1.14\end{aligned}$$

The experimental value is 1.18 [12] for an error of -3.4%.

In Figure 11-1 a comparison is shown between calculated and experimental activity coefficients over the entire range of compositions. The left-most experimental value for the activity coefficient of *n*-pentane almost certainly illustrates the difficulty of measuring the activity coefficient at low concentration.

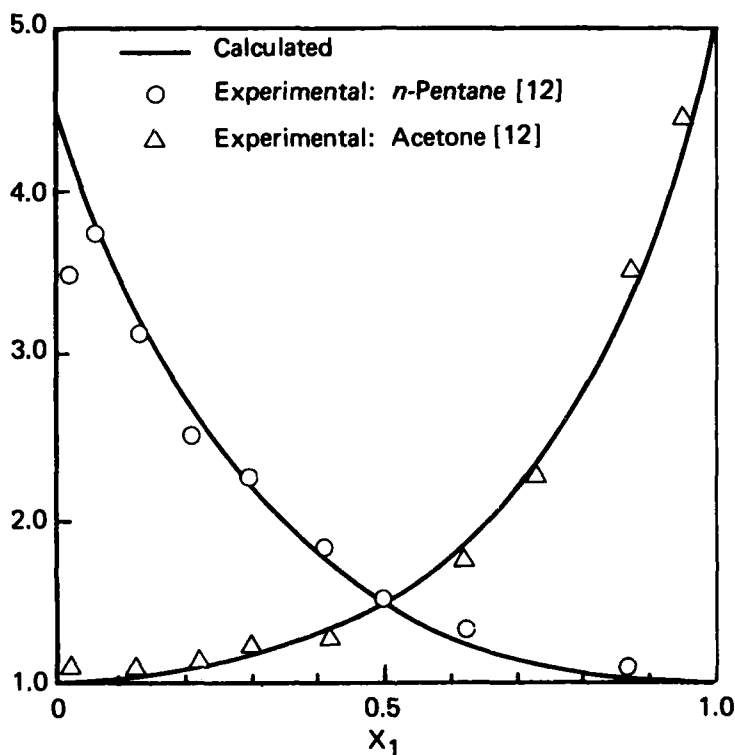
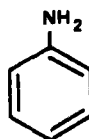


FIGURE 11-1 Calculated Activity Coefficients in the System *n*-Pentane-Acetone at 760 mm Hg

The *n*-pentane-acetone system is not too far removed from ideal behavior, and the Van Laar equation may be used to calculate the vapor-liquid equilibrium. This was done following the procedure outlined in Reid *et al.* [21] and using Method 2 of Chapter 14 to estimate pure-component vapor pressures. Figure 11-2 shows the results obtained.

Example 11-4 Estimate the infinite-dilution activity coefficient of aniline in water at 25°C.

(1) The structure of aniline is



11-19

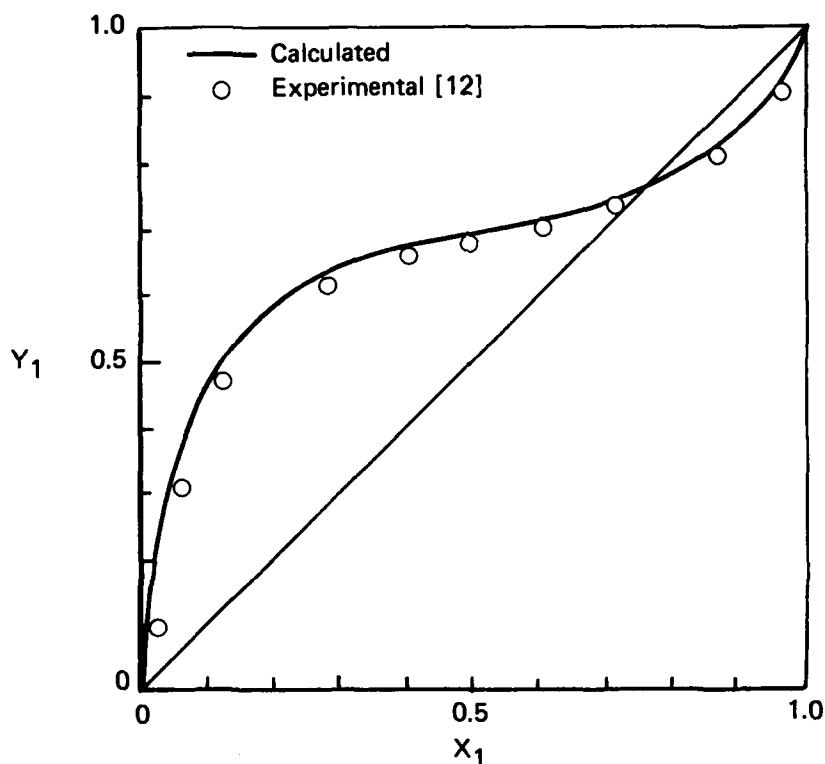


FIGURE 11-2 Calculated vs. Experimental Vapor-Liquid Equilibrium in the System n-Pentane-Acetone at 760 mm Hg

- (2) In Example 11-2 the $\log \gamma_1^\infty$ for benzene in water was estimated to be 3.321.
- (3) From Table 11-5 the correction factor for the NH_2 group is -1.35.
- (4) Thus for aniline

$$\log \gamma_1^\infty = (\log \gamma_1^\infty)_{\text{benzene}} - 1.35 = 1.971$$

$$\gamma_1^\infty = 94$$

The experimental value is 120 [25] for an error of -22%.

11-5 METHOD 2 — UNIFAC

The UNIFAC method is a group contribution concept. The basic idea is that, whereas there are thousands of organic compounds, the number of functional groups that constitute these compounds is much smaller.

Estimation of thermodynamic properties of liquid mixtures from group contributions was first suggested by Langmuir [11]. This suggestion received little attention until Derr *et al.* [5,6] used group contributions to correlate heats of mixing, followed by Wilson and Deal [28], who developed the "solution of groups" method for activity coefficients.

The basic aim of the solution of groups method is to utilize existing phase equilibrium data for predicting phase equilibria of systems for which there are no experimental data. The method entails suitable reduction of experimental data to obtain parameters characteristic of certain groups. These parameters can then be used in other systems containing these groups. A group is defined as any convenient structural fragment — CH_3 , CH_2OH , COOH , CH_2Cl , etc.

The primary feature of all solution-of-group methods is that the logarithm of the activity coefficient is assumed to be the sum of two contributions — a combinatorial part, essentially due to differences in size and shape of the molecules in the mixture, and a residual part, essentially due to energy interactions. Thus, for molecule i in any solution:

$$\ln \gamma_i = \underbrace{\ln \gamma_i^C}_{\text{combinatorial}} + \underbrace{\ln \gamma_i^R}_{\text{residual}} \quad (11-15)$$

In the ASOG method, developed by Wilson and Deal [28], the combinatorial part is given by the athermal Flory-Huggins [10] equation, and the residual part is given by the Wilson equation. The practical application of ASOG has been discussed by Palmer [17].

In UNIFAC the combinatorial part of Eq. 11-15 is given [9] for a binary mixture by

$$\ln \gamma_1^C = \ln \frac{\phi_1}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\phi_1} + \ell_1 - \frac{\phi_1}{x_1} (x_1 \ell_1 + x_2 \ell_2) \quad (11-16)$$

and

$$\ln \gamma_2^C = \ln \frac{\phi_2}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2}{\phi_2} + \ell_2 - \frac{\phi_2}{x_2} (x_1 \ell_1 + x_2 \ell_2) \quad (11-17)$$

where

$$\phi_1 = \frac{r_1 x_1}{r_1 x_1 + r_2 x_2} \quad \theta_1 = \frac{q_1 x_1}{q_1 x_1 + q_2 x_2} \quad (11-18a)$$

$$\phi_2 = \frac{r_2 x_2}{r_1 x_1 + r_2 x_2} \quad \theta_2 = \frac{q_2 x_2}{q_1 x_1 + q_2 x_2} \quad (11-18b)$$

Note that $\phi_1 + \phi_2 = 1$ and $\theta_1 + \theta_2 = 1$.

$$\left. \begin{aligned} \ell_1 &= \frac{z}{2} (r_1 - q_1) - (r_1 - 1) & ; & \quad z = 10 \\ \ell_2 &= \frac{z}{2} (r_2 - q_2) - (r_2 - 1) \end{aligned} \right\} \quad (11-19)$$

$$\left. \begin{aligned} r_1 &= \sum_k \nu_k^{(1)} R_k & ; & \quad r_2 = \sum_k \nu_k^{(2)} R_k \\ q_1 &= \sum_k \nu_k^{(1)} Q_k & ; & \quad q_2 = \sum_k \nu_k^{(2)} Q_k \end{aligned} \right\} \quad (11-20)$$

and where

- x_1, x_2 = mole fraction of components 1 and 2
- ν_k = 1, 2, . . . N (number of groups in molecule 1 or 2)
- R_k = the van der Waals volume for group k
- Q_k = the van der Waals surface area for group k
- k = group number (assigned) from Table 11-6

In Table 11-6 group volumes and surface areas are given for the 25 main groups that have been studied to date. Note that the main group often contains subgroups with different R_k and Q_k values. These classifications are based on experience gained from fitting the UNIFAC model to vapor-liquid equilibrium data.⁶

6. [Note added in final proof.] A new set of UNIFAC parameters (R_k , Q_k and a_{mn} values) has recently been published (Magnussen *et al.*, *Ind. Eng. Chem. Process Des. Dev.*, **20**, 331-339, 1981). The new parameters were determined from binary and ternary liquid-liquid equilibrium data sets rather than vapor-liquid equilibrium data. The new parameters are definitely preferable for solubility calculations (methods of Chapter 3) or other predictions of liquid-liquid equilibria since the method errors will generally be lower. The new parameters should not be used for components with normal boiling points below 300K nor should they be used outside the temperature range of 10 to 40°C. See J. Gmehling *et al.*, *Ind. Eng. Chem. Process Des. Dev.*, **21**:118 (1982) for new set of parameters.

TABLE 11-6

Group Volume and Surface-Area Parameters

Main Group	Subgroup ^a	k	R _k	Q _k	Sample Group Assignment
1 "CH ₂ "	CH ₃	1	0.9011	0.848	Butane: 2 CH ₃ , 2 CH ₂
	CH ₂	2	0.6744	0.540	
	CH	3	0.4469	0.228	2-Methylpropane: 3 CH ₃ , 1 CH
	C	4	0.2195	0.000	2,2-Dimethylpropane: 4 CH ₃ , 1 C
2 "C=C"	CH ₂ =CH	5	1.3454	1.176	1-Hexene: 1 CH ₃ , 3 CH ₂ , 1 CH ₂ =CH
	CH=CH	6	1.1167	0.867	2-Hexene: 2 CH ₃ , 2 CH ₂ , 1 CH=CH
	CH=C	7	0.8886	0.676	2-Methyl-2-butene: 3 CH ₃ , 1 CH=C
	CH ₂ =C	8	1.1173	0.988	2-Methyl-1-butene: 2 CH ₃ , 1 CH ₂ , 1 CH ₂ =C
3 "ACH"	ACH	9	0.5313	0.400	Benzene: 6 ACH
	AC	10	0.3652	0.120	Styrene: 1 CH ₂ =CH, 5 ACH, 1 AC
4 "ACCH ₂ "	ACCH ₃	11	1.2663	0.968	Toluene: 5 ACH, 1 ACCH ₃
	ACCH ₂	12	1.0396	0.660	Ethylbenzene: 1 CH ₃ , 5 ACH, 1 ACCH ₂
	ACCH	13	0.8121	0.348	Cumene: 2 CH ₃ , 5 ACH, 1 ACCH
5 "OH"	OH	14	1.000	1.200	1-Propanol: 1 CH ₃ , 2 CH ₂ , 1 OH
6	CH ₃ OH	15	1.4311	1.432	Methanol: 1 CH ₃ OH
7	H ₂ O	16	0.92	1.40	Water: 1 H ₂ O
8	ACOH	17	0.8952	0.680	Phenol: 5 ACH, 1 ACOH
9 "CH ₂ CO"	CH ₃ CO	18	1.6724	1.488	Ketone group is 2nd carbon; 2-Butanone: 1 CH ₃ , 1 CH ₂ , 1 CH ₃ CO
	CH ₂ CO	19	1.4457	1.180	Ketone group is any other carbon; 3-Pentanone: 2 CH ₃ , 1 CH ₂ , 1 CH ₂ CO
10	CHO	20	0.9980	0.948	Acetaldehyde: 1 CH ₃ , 1 CHO
11 "COOC"	CH ₃ COO	21	1.9031	1.728	Butyl acetate: 1 CH ₃ , 3 CH ₂ , 1 CH ₃ COO
	CH ₂ COO	22	1.6764	1.420	Butyl propanoate: 2 CH ₃ , 3 CH ₂ , 1 CH ₂ COO
12 "CH ₂ O"	CH ₃ O	23	1.1450	1.088	Dimethyl ether: 1 CH ₃ , 1 CH ₃ O
	CH ₂ O	24	0.9183	0.780	Diethyl ether: 2 CH ₃ , 1 CH ₂ , 1 CH ₂ O
	CH-O	25	0.6908	0.468	Diisopropyl ether: 4 CH ₃ , 1 CH, 1 CH-O
	FCH ₂ O	26	0.9183	1.1	Tetrahydrofuran: 3 CH ₂ , 1 FCH ₂ O
13 "CNH ₂ "	CH ₃ NH ₂	27	1.5959	1.544	Methylamine: 1 CH ₃ NH ₂
	CH ₂ NH ₂	28	1.3692	1.236	Propylamine: 1 CH ₃ , 1 CH ₂ , 1 CH ₂ NH ₂
	CHNH ₂	29	1.1417	0.924	Isopropylamine: 2 CH ₃ , 1 CHNH ₂
14 "CNH"	CH ₃ NH	30	1.4337	1.244	Dimethylamine: 1 CH ₃ , 1 CH ₃ NH
	CH ₂ NH	31	1.2070	0.936	Diethylamine: 2 CH ₃ , 1 CH ₂ , 1 CH ₂ NH
	CHNH	32	0.9795	0.624	Diisopropylamine: 4 CH ₃ , 1 CH, 1 CHNH
15	ACNH ₂	33	1.0600	0.816	Aniline: 5 ACH, 1 ACNH ₂
16 "CCN"	CH ₃ CN	34	1.8701	1.724	Acetonitrile: 1 CH ₃ CN
	CH ₂ CN	35	1.6434	1.416	Propionitrile: 1 CH ₃ , 1 CH ₂ CN
17 "COOH"	COOH	36	1.3013	1.224	Acetic acid: 1 CH ₃ , 1 COOH
	HCOOH	37	1.5280	1.532	Formic acid: 1 HCOOH
18 "CCI"	CH ₂ Cl	38	1.4654	1.264	1-Chlorobutane: 1 CH ₃ , 2 CH ₂ , 1 CH ₂ Cl
	CHCl	39	1.2380	0.952	2-Chloropropane: 2 CH ₃ , 1 CHCl
	CCl	40	1.0060	0.724	2-Chloro-2-methylpropane: 3 CH ₃ , 1 CCl
19 "CCl ₂ "	CH ₂ Cl ₂	41	2.2564	1.988	Dichloromethane: 1 CH ₂ Cl ₂
	CHCl ₂	42	2.0606	1.684	1,1-Dichloroethane: 1 CH ₃ , 1 CHCl ₂
	CCl ₂	43	1.8016	1.448	2,2-Dichloropropane: 2 CH ₃ , 1 CCl ₂

(continued)

TABLE 11-6 (Continued)

Main Group	Subgroup ^a	k	R _k	Q _k	Sample Group Assignment
20 "CCl ₃ "	CHCl ₃	44	2.8700	2.410	Chloroform: 1 CHCl ₃
	CCl ₃	45	2.6401	2.184	1,1,1-Trichloroethane: 1 CH ₃ , 1 CCl ₃
21	CCl ₄	46	3.3900	2.910	Tetrachloromethane: 1 CCl ₄
22	ACCl	47	1.1562	0.844	Chlorobenzene: 5 ACH, 1 ACCl
23 "CNO ₂ "	CH ₃ NO ₂	48	2.0086	1.868	Nitromethane: 1 CH ₃ NO ₂
	CH ₂ NO ₂	49	1.7818	1.560	1-Nitropropane: 1 CH ₃ , 1 CH ₂ , 1 CH ₂ NO ₂
	CHNO ₂	50	1.5544	1.248	2-Nitropropane: 2 CH ₃ , 1 CHNO ₂
24	ACNO ₂	51	1.4199	1.104	Nitrobenzene: 5 ACH, 1 ACNO ₂
25	CS ₂	52	2.057	1.65	Carbon disulfide: 1 CS ₂
26 "(C) ₃ N"	CH ₃ N	53	1.187	0.940	Trimethylamine: 2 CH ₃ , 1 CH ₃ N
	CH ₂ N	54	0.9598	0.632	Triethylamine: 3 CH ₃ , 2 CH ₂ , 1 CH ₂ N
27 "HCOO"	HCOO	55	1.242	1.188	Ethyl formate: 1 CH ₃ , 1 CH ₂ , 1 HCOO
28 "I"	I	56	1.264	0.992	Iodoethane: 1 CH ₃ , 1 CH ₂ , 1 I ₂
29 "Br"	Br	57	0.9492	0.832	Bromo methane: 1 CH ₃ , 1 Br
30 "CH ₃ SH"	CH ₃ SH	58	1.877	1.676	Methanethiol: 1 CH ₃ SH
31 "CCOH"	CCOH	59	--	--	--
32 "Furfural"	Furfural	60	3.168	2.484	Furfural: 1 Furfural
33 "Pyridine"	C ₅ H ₅ N	61	2.9993	2.113	Pyridine: 1 C ₅ H ₅ N
	C ₄ H ₄ N	62	2.8832	1.833	3-methyl pyridine: 1 CH ₃ , 1 C ₄ H ₄ N
	C ₅ H ₄ N	63	2.667	1.558	2,3-methyl pyridine: 2 CH ₃ , 1 C ₅ H ₄ N
34 "DOH"	(CH ₂ OH) ₂	64	2.4088	2.248	1,2 ethanediol: 1 (CH ₂ OH) ₂

a. "A" refers to an aromatic ring.

Sources: Fredenslund, Gmehling and Rasmussen [8], and
Skjold-Jørgensen, Kolbe, Gmehling and Rasmussen [24].

For a binary mixture, the residual part of Eq. 11-15 is given by:

$$\left. \begin{aligned} \ln \gamma_1^R &= \sum_k \nu_k^{(1)} [\ln \Gamma_k - \ln \Gamma_k^{(1)}] \\ \ln \gamma_2^R &= \sum_k \nu_k^{(2)} [\ln \Gamma_k - \ln \Gamma_k^{(2)}] \end{aligned} \right\} \quad (11-21)$$

where

$$\ln \Gamma_k = Q_k [1 - \ln (\sum_m \Theta_m \psi_{mk}) - \sum_m (\Theta_m \psi_{km} / \sum_n \Theta_n \psi_{nm})] \quad (11-22)$$

and m and $n = 1, 2, \dots, N$ (all groups)

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad X_m = \frac{\sum_j \nu_m^{(j)} x_j}{\sum_j \sum_n \nu_n^{(j)} x_j} \quad (11-23)$$

$j = 1, 2, \dots, M$; $n = 1, 2, \dots, N$

Similar relationships hold for $\ln \Gamma_k^{(1)}$ and $\ln \Gamma_k^{(2)}$. Note, however, that these refer to the pure components.

Furthermore,

- j = component number (1 or 2 for a binary mixture)
- M = total number of components (= 2 for a binary mixture)
- n = group number
- N = total groups
- Θ_m = group surface area fraction
- X_m = group fraction (For example, for an equimolar mixture of butane and hexane, the group fractions for CH_3 and CH_2 are 4/10 and 6/10, respectively.)
- x_j = mole fraction of molecule j in the mixture
- $\nu_m^{(j)}$ = number of groups of type m in molecule j
- $\psi_{nm} = \exp(-a_{nm}/T)$
- T = temperature (K)

(11-24)

The parameter a_{nm} is a group interaction parameter which is a measure of the difference in interaction energy between groups n and m . In general, a_{nm} is independent of temperature and $a_{nm} \neq a_{mn}$. The interaction parameters have been determined for 34 groups covering a large number of compounds, and are reproduced from Ref. 24 as Table 11-7. Notice that, with respect to a_{nm} , the 34 main groups are not broken down into subgroups as was done for the van der Waals surface areas and volumes.

Basic Steps

- (1) Draw the structures of the chemicals involved.
- (2) Determine the kind and number of structural groups corresponding to those represented in Table 11-6. (See footnote 6, p. 11-22.)

TABLE 11-7

UNIFAC Group Interaction Parameters a_{mn}
(m indicates row, n indicates column)^a

		1 CH ₂	2 C=C	3 ACH	4 ACCH ₂	5 OH
1	CH ₂	0	-200.0	61.13	76.50	986.5
2	C=C	2520	0	340.7	4102	693.9
3	ACH	-11.12	-94.78	0	167.0	636.1
4	ACCH ₂	-69.70	-269.7	-146.8	0	803.2
5	OH	156.4	8694	89.60	25.82	0
6	CH ₃ OH	16.51	-52.39	-50.00	-44.50	249.1
7	H ₂ O	300.0	692.7	362.3	377.6	-229.1
8	ACOH	311.0	n.a.	2043	6245	-533.0
9	CH ₂ CO	26.76	-82.92	140.1	365.8	164.5
10	CHO	505.7	n.a.	n.a.	n.a.	-404.8 ^c
11	COOC	114.8	n.a.	85.84	-170.0	245.4
12	CH ₂ O	83.36	76.44	52.13	65.69	237.7
13	CNH ₂	-30.48	79.40	-44.85	n.a.	-164.0
14	CNH	65.33	-41.32	-22.31	223.0	-150.0
15	ACNH ₂	5339	n.a.	650.4	979.8	529.0
16	CCN	24.82	34.78	-22.97	-138.4	185.4
17	COOH	315.3	349.2	62.32	268.2	-151.0
18	CCI	91.46	-24.36	4.680	122.9	562.2
19	CCl ₂	34.01	-52.71	n.a.	n.a.	747.7
20	CCl ₃	36.70	-185.1	288.5	33.61	742.1
21	CCl ₄	-78.45	-293.7	-4.700	134.7	856.3
22	ACCI	-141.3	n.a.	-237.7	375.5	246.9
23	CNO ₂	-32.69	-49.92	10.38	-97.05	341.7 ^c
24	ACNO ₂	5541	n.a.	1825	n.a.	n.a.
25	CS ₂	-52.65	16.62	21.50	40.68	823.5
26	(C) ₃ N	-83.98	-188.0	-223.9	n.a.	28.60
27	HCOO	90.49	n.a.	n.a.	n.a.	191.2
28	I	128.0	n.a.	58.68	n.a.	501.3
29	Br	-31.52	n.a.	155.6	291.1	721.9
30	CH ₃ SH	-7.481	n.a.	28.41	n.a.	461.6 ^c
31	CCOH	-87.93	121.5	-64.13	-99.38	n.a.
32	Furfural	-25.31	n.a.	157.3	404.3	521.6
33	Pyridine	-101.6	n.a.	31.87	49.80	-132.3
34	DOH	140.0	n.a.	221.4	150.6	267.6

(Continued)

TABLE II-7 (Continued)

		6 CH ₃ OH	7 H ₂ O	8 ACOH	9 CH ₂ CO	10 CHO
1	CH ₂	697.2	1318	2789	476.4	677.0
2	C=C	1509	634.2	n.a.	524.5	n.a.
3	ACH	637.4	903.8	1397.0	25.77	n.a.
4	ACCH ₂	603.3	5695.0	726.3	-52.10	n.a.
5	OH	-137.1	353.5	286.3	84.00	441.8 ^c
6	CH ₃ OH	0	-181.0	(n.a.)	23.39	306.4
7	H ₂ O	289.6	0	442.0	-195.4	-257.3
8	ACOH	(n.a.)	-540.6	0	n.a.	n.a.
9	CH ₂ CO	108.7	472.5	n.a.	0	-37.36
10	CHO	-340.2	232.7	n.a.	128.0	0
11	COOC	249.6	10000	853.6	372.2	n.a.
12	CH ₂ O	339.7	-314.7	n.a.	52.38	n.a.
13	CNH ₂	-481.7	-330.4	n.a.	n.a.	n.a.
14	CNH	-500.4	-448.2 ^d	n.a.	n.a.	n.a.
15	ACNH ₂	(n.a.)	-339.5	n.a.	n.a.	n.a.
16	CCN	157.8	242.8	n.a.	-287.5	n.a.
17	COOH	1020	-66.17	n.a.	-297.8	n.a.
18	CCl	529.0	698.2	n.a.	286.3	-47.51
19	CCl ₂	669.9	708.7	n.a.	423.2	n.a.
20	CCl ₃	649.1	826.8	n.a.	552.1	n.a.
21	CCl ₄	860.1	1201	1616	372.0	n.a.
22	ACCl	(n.a.)	920.4	n.a.	n.a.	n.a.
23	CNO ₂	252.6	417.9	n.a.	-142.6	n.a.
24	ACNO ₂	n.a.	360.7	n.a.	n.a.	n.a.
25	CS ₂	914.2	1081	n.a.	303.7	n.a.
26	(C) ₃ N	(n.a.)	-598.8 ^d	n.a.	n.a.	n.a.
27	HCOO	155.7	n.a.	n.a.	n.a.	n.a.
28	I	(n.a.)	n.a.	n.a.	138.0	n.a.
29	Br	(n.a.)	n.a.	n.a.	-142.6	n.a.
30	CH ₃ SH	382.8	n.a.	n.a.	160.6	n.a.
31	CCOH	127.4	60.81	257.3	48.16	n.a.
32	Furfural	(n.a.)	23.48	n.a.	317.5	n.a.
33	Pyridine	-378.2	-332.9	-222.2	n.a.	n.a.
34	DOH	(n.a.)	n.a.	523.0	n.a.	n.a.

(Continued)

TABLE 11-7 (Continued)

		11 COOC	12 CH ₂ O	13 CNH ₂	14 CNH	15 ACNH ₂
1	CH ₂	232.1	251.5	391.5	255.7	1245
2	C=C	n.a.	289.3	396.0	273.6	n.a.
3	ACH	5.994	32.14	161.7	122.8	668.2
4	ACCH ₂	5688	213.1	n.a.	-49.29	764.7
5	OH	101.1	28.06	83.02	42.70	-348.2
6	CH ₃ OH	-10.72	-180.6	359.3	266.0	(n.a.)
7	H ₂ O	14.42	540.5 ^d	48.89	168.0 ^d	213.0
8	ACOH	-713.2	n.a.	n.a.	n.a.	n.a.
9	CH ₂ CO	-213.7	5.202	n.a.	n.a.	n.a.
10	CHO	n.a.	n.a.	n.a.	n.a.	n.a.
11	COOC	0	-235.7	n.a.	-73.50	n.a.
12	CH ₂ O	461.3	0	n.a.	141.7	n.a.
13	CNH ₂	n.a.	n.a.	0	63.72	n.a.
14	CNH	136.0	-49.30	108.8	0	n.a.
15	ACNH ₂	n.a.	n.a.	n.a.	n.a.	0
16	CCN	-266.6	n.a.	n.a.	n.a.	n.a.
17	COOH	-256.3	-338.5	n.a.	n.a.	n.a.
18	CCl	n.a.	225.4	n.a.	n.a.	n.a.
19	CCl ₂	-132.9	-197.7	n.a.	n.a.	n.a.
20	CCl ₃	176.5	-20.93	n.a.	n.a.	n.a.
21	CCl ₄	129.5	113.9	n.a.	91.13	1302
22	ACCl	-246.3	n.a.	203.5	-108.4	n.a.
23	CNO ₂	n.a.	-94.49	n.a.	n.a.	n.a.
24	ACNO ₂	n.a.	n.a.	n.a.	n.a.	5250
25	CS ₂	243.8	112.4	n.a.	n.a.	n.a.
26	(C) ₃ N	n.a.	n.a.	n.a.	n.a.	n.a.
27	HCOO	-261.1	n.a.	n.a.	n.a.	n.a.
28	I	21.92	474.6	n.a.	n.a.	n.a.
29	Br	n.a.	n.a.	n.a.	n.a.	n.a.
30	CH ₃ SH	n.a.	63.71	106.7	n.a.	n.a.
31	CCOH	76.20	70.00	110.8	188.3	412.0
32	Furfural	-146.3	n.a.	n.a.	n.a.	n.a.
33	Pyridine	n.a.	n.a.	n.a.	n.a.	n.a.
34	DOH	n.a.	n.a.	n.a.	n.a.	164.4

(Continued)

TABLE 11-7 (Continued)

		16 CCN	17 COOH	18 CCl	19 CCl ₂	20 CCl ₃
1	CH ₂	597.0	663.5	35.93	53.76	24.9
2	C=C	405.9	730.4	99.61	337.1	4583
3	ACH	212.5	537.4	-18.81	n.a.	-231.9
4	ACCH ₂	6096	603.8	-114.1	n.a.	-12.14
5	OH	6.712	199.0	75.62	-112.1	-98.12
6	CH ₃ OH	36.23	-289.5	-38.32	-102.5	-139.4
7	H ₂ O	112.6	-14.09	325.4	370.4	353.7
8	ACOH	n.a.	n.a.	n.a.	n.a.	n.a.
9	CH ₂ CO	481.7	669.4	-191.7	-284.0	-354.6
10	CHO	n.a.	n.a.	751.8	n.a.	n.a.
11	COOC	494.6	660.2	n.a.	108.9	-209.7
12	CH ₂ O	n.a.	664.6	301.1	137.8	-154.3
13	CNH ₂	n.a.	n.a.	n.a.	n.a.	n.a.
14	CNH	n.a.	n.a.	n.a.	n.a.	n.a.
15	ACNH ₂	n.a.	n.a.	n.a.	n.a.	n.a.
16	CCN	0	n.a.	n.a.	n.a.	-15.62
17	COOH	n.a.	0	44.42	-183.4	n.a.
18	CCl	n.a.	326.4	0	108.3	249.2
19	CCl ₂	n.a.	1821	-84.53	0	0
20	CCl ₃	74.04	n.a.	-157.1	0	0
21	CCl ₄	492.0	689.0	11.80	17.97	51.90
22	ACCl	n.a.	n.a.	n.a.	n.a.	n.a.
23	CNO ₂	n.a.	n.a.	n.a.	n.a.	n.a.
24	ACNO ₂	n.a.	n.a.	n.a.	n.a.	n.a.
25	CS ₂	335.7	n.a.	-73.09	n.a.	-26.06
26	(C) ₃ N	n.a.	n.a.	n.a.	-73.87	-352.9
27	HCOO	n.a.	-356.3	n.a.	n.a.	n.a.
28	I	n.a.	n.a.	n.a.	-40.82	21.76
29	Br	n.a.	n.a.	1169	n.a.	n.a.
30	CH ₃ SH	125.7	n.a.	-27.94	n.a.	n.a.
31	CCOH	n.a.	77.61	-38.23	-185.9	-170.9
32	Furfural	n.a.	n.a.	n.a.	n.a.	48.30
33	Pyridine	-169.7	n.a.	n.a.	n.a.	-114.7
34	DOH	n.a.	n.a.	n.a.	n.a.	n.a.

(Continued)

TABLE 11-7 (Continued)

		21 CCl ₄	22 ACCl	23 CNO ₂	24 ACNO ₂	25 CS ₂
1	CH ₂	104.3	321.5	661.5	543.0	153.6
2	C=C	5831	n.a.	542.1	n.a.	76.30
3	ACH	3.000	538.2	168.1	194.9	52.07
4	ACCH ₂	-141.3	-126.9	3629	n.a.	-9.450
5	OH	143.1	287.8	61.11 ^c	n.a.	477.0
6	CH ₃ OH	-67.80	(n.a.)	75.14	n.a.	-31.09
7	H ₂ O	497.5	678.2	220.6	399.5	887.1
8	ACOH	4894	n.a.	n.a.	n.a.	n.a.
9	CH ₂ CO	-39.20	n.a.	137.5	n.a.	216.1
10	CHO	n.a.	n.a.	n.a.	n.a.	n.a.
11	COOC	54.47	629.0	n.a.	n.a.	183.0
12	CH ₂ O	47.67	n.a.	95.18	n.a.	140.9
13	CNH ₂	n.a.	68.81	n.a.	n.a.	n.a.
14	CNH	71.23	4350	n.a.	n.a.	n.a.
15	ACNH ₂	8455	n.a.	n.a.	-62.73	n.a.
16	CCN	-54.86	n.a.	n.a.	n.a.	230.9
17	COOH	212.7	n.a.	n.a.	n.a.	n.a.
18	CCl	62.42	n.a.	n.a.	n.a.	450.1
19	CCl ₂	56.33	n.a.	n.a.	n.a.	n.a.
20	CCl ₃	-30.10	n.a.	n.a.	n.a.	116.6
21	CCl ₄	0	475.8	490.9	534.7	132.2
22	ACCl	-255.4	0	-154.5	n.a.	n.a.
23	CNO ₂	-34.68	794.4	0	n.a.	n.a.
24	ACNO ₂	514.6	n.a.	n.a.	0	n.a.
25	CS ₂	-60.71	n.a.	n.a.	n.a.	0
26	(C) ₃ N	-8.283	-86.36	n.a.	n.a.	n.a.
27	HCOO	n.a.	n.a.	n.a.	n.a.	n.a.
28	I	48.49	n.a.	n.a.	n.a.	n.a.
29	Br	225.8	224.0	125.3	n.a.	n.a.
30	CH ₃ SH	n.a.	n.a.	n.a.	n.a.	n.a.
31	CCOH	-98.66	290.0	n.a.	n.a.	73.52
32	Furfural	-133.2	n.a.	n.a.	n.a.	n.a.
33	Pyridine	n.a.	n.a.	n.a.	n.a.	n.a.
34	DOH	n.a.	n.a.	481.3	n.a.	n.a.

(Continued)

TABLE 11-7 (Continued)

		26 (C) ₃ N	27 HCOO	28 I	29 Br	30 CH ₃ SH ^b
1	CH ₂	206.6	741.4	335.8	479.5	184.4
2	C=C	658.8	n.a.	n.a.	n.a.	n.a.
3	ACH	90.49	n.a.	113.3	-13.59	-10.43
4	ACCH ₂	n.a.	n.a.	n.a.	-171.3	n.a.
5	OH	-323.0	193.1	313.5	133.4	14.75 ^c
6	CH ₃ OH	(n.a.)	193.4	(n.a.)	(n.a.)	37.84
7	H ₂ O	304.0 ^d	n.a.	n.a.	n.a.	n.a.
8	ACOH	n.a.	n.a.	n.a.	n.a.	n.a.
9	CH ₂ CO	n.a.	n.a.	53.59	245.2	-46.28
10	CHO	n.a.	n.a.	n.a.	n.a.	n.a.
11	COOC	n.a.	372.9	148.3	n.a.	n.a.
12	CH ₂ O	n.a.	n.a.	-149.5	n.a.	-8.538
13	CNH ₂	n.a.	n.a.	n.a.	n.a.	-70.14
14	CNH	n.a.	n.a.	n.a.	n.a.	n.a.
15	ACNH ₂	n.a.	n.a.	n.a.	n.a.	n.a.
16	CCN	n.a.	n.a.	n.a.	n.a.	21.37
17	COOH	n.a.	312.5	n.a.	n.a.	n.a.
18	CCl	n.a.	n.a.	n.a.	-125.9	59.02
19	CCl ₂	-141.4	n.a.	177.6	n.a.	n.a.
20	CCl ₃	-293.7	n.a.	86.40	n.a.	n.a.
21	CCl ₄	-126.0	n.a.	247.8	41.94	n.a.
22	ACCl	1088	n.a.	n.a.	-60.70	n.a.
23	CNO ₂	n.a.	n.a.	n.a.	10.17	n.a.
24	ACNO ₂	n.a.	n.a.	n.a.	n.a.	n.a.
25	CS ₂	n.a.	n.a.	n.a.	n.a.	n.a.
26	(C) ₃ N	0	n.a.	n.a.	n.a.	n.a.
27	HCOO	n.a.	0	n.a.	n.a.	4.339
28	I	n.a.	n.a.	0	n.a.	n.a.
29	Br	n.a.	n.a.	n.a.	0	n.a.
30	CH ₃ SH	n.a.	239.8	n.a.	n.a.	0
31	CCOH	n.a.	n.a.	n.a.	n.a.	n.a.
32	Furfural	n.a.	n.a.	n.a.	n.a.	n.a.
33	Pyridine	n.a.	n.a.	n.a.	n.a.	n.a.
34	DOH	n.a.	n.a.	n.a.	n.a.	n.a.

(Continued)

TABLE 11-7 (Continued)

		31 CCOH	32 Furfural	33 Pyridine	34 DOH
1	CH ₂	737.5	354.6	287.8	3025
2	C=C	535.2	n.a.	n.a.	n.a.
3	ACH	477.0	-64.69	-4.449	210.4
4	ACCH ₂	469.0	-20.36	52.80	4975
5	OH	n.a.	-120.5	170.0	-319.0
6	CH ₃ OH	-80.78	(n.a.)	580.5	(n.a.)
7	H ₂ O	43.31	188.0	459.0	n.a.
8	ACOH	-455.4	n.a.	-637.3	-538.6
9	CH ₂ CO	129.2	-163.7	n.a.	n.a.
10	CHO	n.a.	n.a.	n.a.	n.a.
11	COOC	109.9	202.3	n.a.	n.a.
12	CH ₂ O	42.00	n.a.	n.a.	n.a.
13	CNH ₂	-217.2	n.a.	n.a.	n.a.
14	CNH	-243.3	n.a.	n.a.	n.a.
15	ACNH ₂	-245.0	n.a.	n.a.	125.3
16	CCN	n.a.	n.a.	134.3	n.a.
17	COOH	-17.59	n.a.	n.a.	n.a.
18	CCl	368.6	n.a.	n.a.	n.a.
19	CCl ₂	601.6	n.a.	n.a.	n.a.
20	CCl ₃	491.1	-64.38	18.98	n.a.
21	CCl ₄	570.7	546.7	n.a.	n.a.
22	ACCl	134.1	n.a.	n.a.	n.a.
23	CNO ₂	n.a.	n.a.	n.a.	139.8
24	ACNO ₂	n.a.	n.a.	n.a.	n.a.
25	CS ₂	442.8	n.a.	n.a.	n.a.
26	(C) ₃ N	n.a.	n.a.	n.a.	n.a.
27	HCOO	n.a.	n.a.	n.a.	n.a.
28	I	n.a.	n.a.	n.a.	n.a.
29	Br	n.a.	n.a.	n.a.	n.a.
30	CH ₃ SH	n.a.	n.a.	n.a.	n.a.
31	CCOH	0	n.a.	n.a.	n.a.
32	Furfural	n.a.	0	n.a.	n.a.
33	Pyridine	n.a.	n.a.	0	n.a.
34	DOH	n.a.	n.a.	n.a.	0

a. n.a. = not available; (n.a.) = not available as a CH₃OH parameter but predictions may be obtained by means of the OH group. Values of s_{mn} are in units of degrees Kelvin.

b. In addition to the tabulated parameters one pair of parameters is available for higher thiols:

$$s_{CH_2,CH_2SH} = 125.3; s_{CH_2SH,CH_2} = 223.3.$$

c. Estimated from CH₃OH data.

d. Predictions not reliable in the whole concentration range.

Source: Skjold-Jørgensen, Kolbe, Gmehling and Rasmussen [24].

- (3) Calculate r_1 , r_2 , q_1 , and q_2 using Eq. set 11-20 and the R_k and Q_k values from Table 11-6. (See footnote 6, p. 11-22.)
- (4) Calculate ρ_1 and ρ_2 from Eq. set 11-19.
- (5) Calculate ϕ_1 , ϕ_2 , θ_1 , and θ_2 from Eq. set 11-18. Note that $\phi_1 + \phi_2 = 1$ and $\theta_1 + \theta_2 = 1$.
- (6) Calculate $\ln \gamma_1^f$ and $\ln \gamma_2^f$ from Eqs. 11-16 and 11-17.
- (7) Calculate Θ_m and X_m for each group, using Eq. 11-23. Note that $\Sigma \Theta_m = \Sigma X_m = 1$.
- (8) Calculate ψ_{mn} for each group using the value of a_{mn} in Table 11-7 and Eq. 11-24. (See footnote 6, p. 11-22.) Note that m and n are *subgroup* numbers. In Table 11-7 only *main* group numbers are listed. Hence, care must be exercised in looking up interaction parameters. For example, $a_{1,18}$ is the interaction parameter for *subgroups* 1 and 18, which belong to the *main* groups 1 and 9, respectively. Hence, in Table 11-7 we would search for the values corresponding to main groups 1 and 9.
- (9) Calculate $\ln \Gamma_k$ and $\ln \Gamma_k^{(j)}$ for each group, using Eq. set 11-22.
- (10) Calculate $\ln \gamma_1^R$ and $\ln \gamma_2^R$ using Eq. set 11-21.
- (11) Calculate $\ln \gamma_1$ and $\ln \gamma_2$ using Eq. 11-15.

Example 11-5 Estimate the activity coefficients for the system acetone(1)-n-pentane(2) at $T = 307K$ and $x_1 = 0.047$ (whence $x_2 = 0.953$).

- (1) The structures are:

acetone $(CH_3)_2C=O$

n-pentane $CH_3(CH_2)_3CH_3$

- (2) Acetone contains one $CH_3C=O$ group and one CH_3 group.

n-Pentane contains two CH_3 groups and three CH_2 groups.

Table 11-8 below lists the appropriate group parameters.

- (3) From Eq. set 11-20

$$r_1 = 1 \times 0.9011 + 1 \times 1.6724 = 2.5735$$

$$q_1 = 1 \times 0.848 + 1 \times 1.488 = 2.336$$

TABLE 11-8

Group Parameters for Example 11-5
(From Table 11-6)

Group	Main Group No.	k	j	ν_k	R_k	Q_k
CH ₃	1	1	1	1	0.9011	0.848
CH ₃ C=O	9	18	1	1	1.6724	1.488
CH ₃	1	1	2	2	0.9011	0.848
CH ₂	1	2	2	3	0.6744	0.540

$$r_2 = 2 \times 0.9011 + 3 \times 0.6744 = 3.8254$$

$$q_2 = 2 \times 0.848 + 3 \times 0.540 = 3.316$$

(4) From Eq. set 11-19

$$l_1 = 5 (2.5735 - 2.336) - 1.5735 = -0.3860$$

$$l_2 = 5 (3.8254 - 3.316) - 2.8254 = -0.2784$$

(5) From Eq. set 11-18 (Note $x_2 = 1 - x_1$)

$$\phi_1 = \frac{2.5735 \times 0.047}{2.5735 \times 0.047 + 3.8254 \times 0.953} = 0.0321$$

$$\phi_2 = 1 - \phi_1 = 0.9679$$

$$\theta_1 = \frac{2.336 \times 0.047}{2.336 \times 0.047 + 3.316 \times 0.953} = 0.0336$$

$$\theta_2 = 1 - \theta_1 = 0.9664$$

(6) From Eqs. 11-16 and 11-17

$$\begin{aligned} \ln \gamma_1^E &= \ln \left(\frac{0.0321}{0.047} \right) + 5 \times 2.336 \times \ln \left(\frac{0.0336}{0.0321} \right) - 0.3860 \\ &\quad - \left(\frac{0.0321}{0.047} \right) \times [0.047 \times (-0.3860) + 0.953 \times (-0.2784)] \\ &= -0.040 \end{aligned}$$

$$\ln \gamma_2^E = \ln \left(\frac{0.9679}{0.953} \right) + 5 \times 3.316 \times \ln \left(\frac{0.9664}{0.9679} \right) - 0.2784$$

$$\begin{aligned}
& - \left(\frac{0.9679}{0.953} \right) \times [0.047 \times (-0.3860) + 0.953 \times (-0.2784)] \\
& = -0.0007
\end{aligned}$$

(7) From Eq. set 11-23 for pure acetone:

$$\begin{aligned}
X_1^{(1)} &= \frac{\nu_1^{(1)} x_1 + \nu_1^{(2)} x_2}{(\nu_1^{(1)} + \nu_2^{(1)} + \nu_{18}^{(1)}) x_1 + (\nu_1^{(2)} + \nu_2^{(2)} + \nu_{18}^{(2)}) x_2} \\
&= \frac{1 \times 1 + 2 \times 0}{(1 + 0 + 1) \times 1 + (2 + 3 + 0) \times 0} = 1/2
\end{aligned}$$

$$\begin{aligned}
X_2^{(1)} &= \frac{\nu_2^{(1)} x_1 + \nu_2^{(2)} x_2}{(\nu_1^{(1)} + \nu_2^{(1)} + \nu_{18}^{(1)}) x_1 + (\nu_1^{(2)} + \nu_2^{(2)} + \nu_{18}^{(2)}) x_2} \\
&= \frac{0 \times 1 + 3 \times 0}{(1 + 0 + 1) \times 1 + (2 + 3 + 0) \times 0} = 0
\end{aligned}$$

$$\begin{aligned}
X_{18}^{(1)} &= \frac{\nu_{18}^{(1)} x_1 + \nu_{18}^{(2)} x_2}{(\nu_1^{(1)} + \nu_2^{(1)} + \nu_{18}^{(1)}) x_1 + (\nu_1^{(2)} + \nu_2^{(2)} + \nu_{18}^{(2)}) x_2} \\
&= \frac{1 \times 1 + 0 \times 0}{(1 + 0 + 1) \times 1 + (2 + 3 + 0) \times 0} = 1/2
\end{aligned}$$

Note, however, that

$$\begin{aligned}
X_{18}^{(1)} &= 1 - (X_1^{(1)} + X_2^{(1)}) \\
&= 1 - 1/2 - 0 = 1/2 \text{ (See Basic Step 7 above.)}
\end{aligned}$$

For pure n-pentane

$$\begin{aligned}
X_1^{(2)} &= \frac{\nu_1^{(1)} x_1 + \nu_1^{(2)} x_2}{(\nu_1^{(1)} + \nu_2^{(1)} + \nu_{18}^{(1)}) x_1 + (\nu_1^{(2)} + \nu_2^{(2)} + \nu_{18}^{(2)}) x_2} \\
&= \frac{1 \times 0 + 2 \times 1}{(1 + 0 + 1) \times 0 + (2 + 3 + 0) \times 1} = 2/5
\end{aligned}$$

$$X_2^{(2)} = \frac{\nu_2^{(1)} x_1 + \nu_2^{(2)} x_2}{(\nu_1^{(1)} + \nu_2^{(1)} + \nu_{18}^{(1)}) x_1 + (\nu_1^{(2)} + \nu_2^{(2)} + \nu_{18}^{(2)}) x_2}$$

$$= \frac{0 \times 0 + 3 \times 1}{(1 + 0 + 1) \times 0 + (2 + 3 + 0) \times 1} = 3/5$$

$$X_{18}^{(2)} = 1 - (X_1^{(2)} + X_2^{(2)}) = 0$$

At $x_1 = 0.047$, $x_2 = 1 - x_1 = 0.953$, and

$$X_1 = \frac{\nu_1^{(1)} x_1 + \nu_1^{(2)} x_2}{(\nu_1^{(1)} + \nu_2^{(1)} + \nu_{18}^{(1)}) x_1 + (\nu_1^{(2)} + \nu_2^{(2)} + \nu_{18}^{(2)}) x_2}$$

$$X_1 = \frac{1 \times 0.047 + 2 \times 0.953}{2 \times 0.047 + 5 \times 0.953} = 0.4019$$

$$X_2 = \frac{\nu_2^{(1)} x_1 + \nu_2^{(2)} x_2}{(\nu_1^{(1)} + \nu_2^{(1)} + \nu_{18}^{(1)}) x_1 + (\nu_1^{(2)} + \nu_2^{(2)} + \nu_{18}^{(2)}) x_2}$$

$$= \frac{0 \times 0.047 + 3 \times 0.953}{2 \times 0.047 + 5 \times 0.953} = 0.5884$$

$$X_{18} = 1 - (X_1 + X_2) = 0.0097$$

For pure acetone:

$$\Theta_1^{(1)} = \frac{Q_1 X_1^{(1)}}{Q_1 X_1^{(1)} + Q_2 X_2^{(1)} + Q_{18} X_{18}^{(1)}}$$

$$= \frac{0.848 \times 1/2}{0.848 \times 1/2 + 0.540 \times 0 + 1.488 \times 1/2} = 0.3630$$

$$\Theta_2^{(1)} = \frac{Q_2 X_2^{(1)}}{Q_1 X_1^{(1)} + Q_2 X_2^{(1)} + Q_{18} X_{18}^{(1)}} = 0$$

$$\Theta_{18}^{(1)} = 1 - (\Theta_1^{(1)} + \Theta_2^{(1)}) = 0.6370$$

Similarly for pure pentane:

$$\Theta_1^{(2)} = \frac{0.848 \times 2/5}{0.848 \times 2/5 + 0.540 \times 3/5 + 1.488 \times 0} = 0.5115$$

$$\Theta_2^{(2)} = \frac{0.540 \times 3/5}{0.848 \times 2/5 + 0.540 \times 3/5 + 1.488 \times 0} = 0.4885$$

$$\Theta_{18}^{(2)} = 1 - (\Theta_1^{(2)} + \Theta_2^{(2)}) = 0$$

At $x_1 = 0.047$

$$\begin{aligned} \Theta_1 &= \frac{Q_1 X_1}{Q_1 X_1 + Q_2 X_2 + Q_{18} X_{18}} \\ &= \frac{0.848 \times 0.4019}{0.848 \times 0.4019 + 0.540 \times 0.5884 + 1.488 \times 0.0097} = 0.5064 \end{aligned}$$

$$\begin{aligned} \Theta_2 &= \frac{Q_2 X_2}{Q_1 X_1 + Q_2 X_2 + Q_{18} X_{18}} \\ &= \frac{0.540 \times 0.5884}{0.848 \times 0.4019 + 0.540 \times 0.5884 + 1.488 \times 0.0097} = 0.4722 \end{aligned}$$

$$\Theta_{18} = 1 - (\Theta_1 + \Theta_2) = 0.0214$$

(8) From Table 11-7 and Eq. 11-24

$$a_{1,2} = a_{2,1} = a_{1,1} = a_{2,2} = a_{18,18} = 0K$$

$$a_{1,18} = a_{2,18} = 476.4K; a_{18,1} = a_{18,2} = 26.76K$$

$$\psi_{1,18} = \psi_{2,18} = \exp [-476.4/307] = 0.2119$$

$$\psi_{18,1} = \psi_{18,2} = \exp [-26.76/307] = 0.9165$$

$$\psi_{1,2} = \psi_{2,1} = \psi_{1,1} = \psi_{2,2} = \psi_{18,18} = 1$$

(9) As the coefficients $\nu_2^{(1)}$ and $\nu_{18}^{(2)}$ are both equal to zero, $\ln \Gamma_2$ and $\ln \Gamma_2^{(1)}$, for component 1, and $\ln \Gamma_{18}$, $\ln \Gamma_{18}^{(2)}$ for component 2 need not be calculated. Thus from Eq. 11-22 for pure acetone:

$$\begin{aligned} \ln \Gamma_1^{(1)} &= Q_1 \left[1 - \ln (\Theta_1^{(1)} \times \psi_{1,1} + \Theta_2^{(1)} \times \psi_{2,1} + \Theta_{18}^{(1)} \times \psi_{18,1}) \right. \\ &\quad \left. - \frac{\Theta_1^{(1)} \times \psi_{1,1}}{\Theta_1^{(1)} \times \psi_{1,1} + \Theta_2^{(1)} \times \psi_{2,1} + \Theta_{18}^{(1)} \times \psi_{18,1}} \right] \end{aligned}$$

$$\begin{aligned}
& - \frac{\Theta_2^{(1)} \times \psi_{1,2}}{\Theta_1^{(1)} \times \psi_{1,2} + \Theta_2^{(1)} \times \psi_{2,2} + \Theta_{18}^{(1)} \times \psi_{18,2}} \\
& - \frac{\Theta_{18}^{(1)} \times \psi_{1,18}}{\Theta_1^{(1)} \times \psi_{1,18} + \Theta_2^{(1)} \times \psi_{2,18} + \Theta_{18}^{(1)} \times \psi_{18,18}} \Big] \\
& = 0.848 \left[1 - \ln (0.3630 \times 1 + 0 \times 1 + 0.6370 \times 0.9165) \right. \\
& - \frac{0.3630 \times 1}{0.3630 \times 1 + 0 \times 1 + 0.6370 \times 0.9165} \\
& - \frac{0 \times 1}{0.3630 \times 1 + 0 \times 1 + 0.6370 \times 0.9165} \\
& \left. - \frac{0.6370 \times 0.2119}{0.3630 \times 0.2119 + 0 \times 0.2119 + 0.6370 \times 1} \right]
\end{aligned}$$

$$= 0.4089$$

$$\begin{aligned}
\ln \Gamma_{18}^{(1)} &= Q_{18} \left[1 - \ln \frac{\Theta_{18}^{(1)} \times \psi_{18,18} + \Theta_1^{(1)} \times \psi_{1,18} + \Theta_2^{(1)} \times \psi_{2,18}}{\Theta_{18}^{(1)} \times \psi_{18,18}} \right. \\
& - \frac{\Theta_1^{(1)} \times \psi_{18,1}}{\Theta_{18}^{(1)} \times \psi_{18,1} + \Theta_1^{(1)} \times \psi_{1,1} + \Theta_2^{(1)} \times \psi_{2,1}} \\
& - \frac{\Theta_2^{(1)} \times \psi_{18,2}}{\Theta_{18}^{(1)} \times \psi_{18,2} + \Theta_1^{(1)} \times \psi_{1,2} + \Theta_2^{(1)} \times \psi_{2,2}} \Big] \\
& = 1.488 \left[1 - \ln (0.6370 \times 1 + 0.3630 \times 0.2119 + 0 \times 0.2119) \right. \\
& - \frac{0.6370 \times 1}{0.6370 \times 1 + 0.3630 \times 0.2119 + 0 \times 0.2119} \\
& - \frac{0.3630 \times 0.9165}{0.6370 \times 0.9165 + 0.3630 \times 1 + 0 \times 1}
\end{aligned}$$

$$- \frac{0 \times 0.9165}{0.6370 \times 0.9165 + 0.3630 \times 1 + 0 \times 1} \Bigg]$$

$$= 0.1389$$

At $x_1 = 0.047$

$$\ln \Gamma_1 = 0.848 \left[1 - \ln (0.5064 \times 1 + 0.4722 \times 1 + 0.0214 \times 0.9165) \right. \\ - \frac{0.5064 \times 1}{0.5064 \times 1 + 0.4722 \times 1 + 0.0214 \times 0.9165} \\ - \frac{0.4722 \times 1}{0.5064 \times 1 + 0.4722 \times 1 + 0.0214 \times 0.9165} \\ \left. - \frac{0.0214 \times 0.2119}{0.5064 \times 0.2119 + 0.4722 \times 0.2119 + 0.0214 \times 1} \right] \\ = 0.0014$$

$$\ln \Gamma_{18} = 1.488 \left[1 - \ln (0.0214 \times 1 + 0.5064 \times 0.2119 + 0.4722 \times 0.2119) \right. \\ - \frac{0.0214 \times 1}{0.0214 \times 1 + 0.5064 \times 0.2119 + 0.4722 \times 0.2119} \\ - \frac{0.5064 \times 0.9165}{0.0214 \times 0.9165 + 0.5064 \times 1 + 0.4722 \times 1} \\ \left. - \frac{0.4722 \times 0.9165}{0.0214 \times 0.9165 + 0.5064 \times 1 + 0.4722 \times 1} \right] \\ = 2.2067$$

From Eq. set 11-21

$$\ln \gamma_1^R = \nu_1^{(1)} (\ln \Gamma_1 - \ln \Gamma_1^{(1)}) + \nu_{18}^{(1)} (\ln \Gamma_{18} - \ln \Gamma_{18}^{(1)}) \\ = 1 \times (0.0014 - 0.4089) + 1 \times (2.2067 - 0.1389) = 1.6603$$

Using Eq. 11-15

$$\ln \gamma_1 = \ln \gamma_1^C + \ln \gamma_1^R \\ = -0.040 + 1.6603 \\ = 1.620$$

$$\gamma_1 = 5.05$$

The experimental value is 4.41 [12] for an error of +14.5%

For pure n-pentane:

$$\ln \Gamma_1^{(2)} = Q_1 \left[1 - \ln(\Theta_1^{(2)} \times \psi_{1,1} + \Theta_2^{(2)} \times \psi_{2,1} + \Theta_{18}^{(2)} \times \psi_{18,1}) \right. \\ \left. - \frac{\Theta_1^{(2)} \times \psi_{1,1}}{\Theta_1^{(2)} \times \psi_{1,1} + \Theta_2^{(2)} \times \psi_{2,1} + \Theta_{18}^{(2)} \times \psi_{18,1}} \right. \\ \left. - \frac{\Theta_2^{(2)} \times \psi_{1,2}}{\Theta_1^{(2)} \times \psi_{1,2} + \Theta_2^{(2)} \times \psi_{2,2} + \Theta_{18}^{(2)} \times \psi_{18,2}} \right. \\ \left. - \frac{\Theta_{18}^{(2)} \times \psi_{1,18}}{\Theta_1^{(2)} \times \psi_{1,18} + \Theta_2^{(2)} \times \psi_{2,18} + \Theta_{18}^{(2)} \times \psi_{18,18}} \right]$$

$$\ln \Gamma_1^{(2)} = 0.848 \left[1 - \ln(0.5115 \times 1 + 0.4885 \times 1 + 0 \times 0.9165) \right. \\ \left. - \frac{0.5115 \times 1}{0.5115 \times 1 + 0.4885 \times 1 + 0 \times 0.9165} \right. \\ \left. - \frac{0.4885 \times 1}{0.5115 \times 1 + 0.4885 \times 1 + 0 \times 0.9165} \right. \\ \left. - \frac{0 \times 0.2119}{0.5115 \times 0.2119 + 0.4885 \times 0.2119 + 0 \times 1} \right] \\ = 0$$

This must be true as pentane contains only one interaction main group, i.e., "CH₂".

Similarly, $\ln \Gamma_2^{(2)} = 0$

At $x_1 = 0.047$

$$\ln \Gamma_1 = Q_1 \left[1 - \ln(\Theta_1 \times \psi_{1,1} + \Theta_2 \times \psi_{2,1} + \Theta_{18} \times \psi_{18,1}) \right. \\ \left. - \frac{\Theta_1 \times \psi_{1,1}}{\Theta_1 \times \psi_{1,1} + \Theta_2 \times \psi_{2,1} + \Theta_{18} \times \psi_{18,1}} \right. \\ \left. - \frac{\Theta_2 \times \psi_{1,2}}{\Theta_1 \times \psi_{1,2} + \Theta_2 \times \psi_{2,2} + \Theta_{18} \times \psi_{18,2}} \right. \\ \left. - \frac{\Theta_{18} \times \psi_{1,18}}{\Theta_1 \times \psi_{1,18} + \Theta_2 \times \psi_{2,18} + \Theta_{18} \times \psi_{18,18}} \right]$$

$$- \frac{\Theta_{18} \times \psi_{1,18}}{\Theta_1 \times \psi_{1,18} + \Theta_2 \times \psi_{2,18} + \Theta_{18} \times \psi_{18,18}} \Bigg]$$

$$\ln \Gamma_1 = 0.848 \left[1 - \ln (0.5064 \times 1 + 0.4722 \times 1 + 0.0214 \times 0.9165) \right.$$

$$- \frac{0.5064 \times 1}{0.5064 \times 1 + 0.4722 \times 1 + 0.0214 \times 0.9165}$$

$$- \frac{0.4722 \times 1}{0.5064 \times 1 + 0.4722 \times 1 + 0.0214 \times 0.9165}$$

$$\left. - \frac{0.0214 \times 0.2119}{0.5064 \times 0.2119 + 0.4722 \times 0.2119 + 0.0214 \times 1} \right]$$

$$= 0.0014$$

$$\ln \Gamma_2 = Q_2 \left[1 - \ln (\Theta_1 \times \psi_{1,2} + \Theta_2 \times \psi_{2,2} + \Theta_{18} \times \psi_{18,2}) \right.$$

$$- \frac{\Theta_1 \times \psi_{2,1}}{\Theta_1 \times \psi_{1,1} + \Theta_2 \times \psi_{2,1} + \Theta_{18} \times \psi_{18,1}}$$

$$- \frac{\Theta_2 \times \psi_{2,2}}{\Theta_1 \times \psi_{1,2} + \Theta_2 \times \psi_{2,2} + \Theta_{18} \times \psi_{18,2}}$$

$$\left. - \frac{\Theta_{18} \times \psi_{2,18}}{\Theta_1 \times \psi_{1,18} + \Theta_2 \times \psi_{2,18} + \Theta_{18} \times \psi_{18,18}} \right]$$

$$\ln \Gamma_2 = 0.540 \left[1 - \ln (0.4722 \times 1 + 0.5064 \times 1 + 0.0214 \times 0.9165) \right.$$

$$- \frac{0.4722 \times 1}{0.4722 \times 1 + 0.5064 \times 1 + 0.0214 \times 0.9165}$$

$$- \frac{0.5064 \times 1}{0.5064 \times 1 + 0.4722 \times 1 + 0.0214 \times 0.9165}$$

$$\left. - \frac{0.0214 \times 0.2119}{0.5064 \times 0.2119 + 0.4722 \times 0.2119 + 0.0214 \times 1} \right]$$

$$= 0.00087$$

$$\ln \gamma_2^R = 2 (0.0014 - 0) + 3 (0.00087 - 0)$$

$$= 0.0054$$

$$\ln \gamma_2 = \ln \gamma_2^C + \ln \gamma_2^R$$

$$= -0.0007 + 0.0266$$

$$= 0.0254$$

$\gamma_2 = 1.005$; the experimental value is 1.08 [12] for an error of -7.0%.

Example 11-6 Estimate the infinite-dilution activity coefficients for the system n-butanol(1)-water(2) at 25°C. From these values, estimate the solubility limit of n-butanol in water.

- (1) The structure of n-butanol is



That for water is H_2O .

- (2) n-Butanol contains one CH_3 group, three CH_2 groups and one OH group. Water contains only the H_2O group. Table 11-9 below lists values of the group parameters.

TABLE 11-9

Group Parameters for Example 11-6
(From Table 11-6)

Group	Main Group No.	k	j	ν_k	R_k	Q_k
CH_3	1	1	1	1	0.9011	0.848
CH_2	1	2	1	3	0.6744	0.540
OH	5	14	1	1	1.000	1.200
H_2O	7	16	2	1	0.920	1.400

As $\nu_1^{(2)}$, $\nu_2^{(2)}$, $\nu_4^{(2)}$ and $\nu_6^{(1)}$ are all equal to zero, no calculations are required for the corresponding $\ln \Gamma_k$ s.

- (3) At infinite dilution Eqs. 11-16 and 11-17 are indeterminate; however, note that at $x_1 = 0$:

$$\frac{\phi_1}{x_1} = \frac{r_1}{r_1 x_1 + r_2 x_2} = \frac{r_1}{r_2}$$

Similar arguments hold for ϕ_2/x_2 , θ_1/ϕ_1 and θ_2/ϕ_2 such that the two equations are altered. For $x_1 = 0$ and $x_2 = 1$, $\ln \gamma_2^c = 0$ and

$$\ln \gamma_1^c = \ln (r_1/r_2) + \frac{z}{2} q_1 \ln \frac{q_1 r_2}{q_2 r_1} + \ell_1 - (r_1/r_2) \ell_2 \quad (11-25)$$

For $x_2 = 0$ and $x_1 = 1$, $\ln \gamma_1^c = 0$ and

$$\ln \gamma_2^c = \ln (r_2/r_1) + \frac{z}{2} q_2 \ln \frac{q_2 r_1}{q_1 r_2} + \ell_2 - (r_2/r_1) \ell_1 \quad (11-26)$$

From Eq. set 11-20

$$r_1 = 1 \times 0.9011 + 3 \times 0.6744 + 1 \times 1.000 = 3.9243$$

$$q_1 = 1 \times 0.848 + 3 \times 0.540 + 1 \times 1.200 = 3.668$$

$$r_2 = 0.92$$

$$q_2 = 1.40$$

From Eq. set 11-19

$$\ell_1 = \frac{10}{2} \times (3.9243 - 3.668) - (3.9243 - 1) = -1.6428$$

$$\ell_2 = -2.32$$

From Eq. 11-25

$$\begin{aligned} \ln \gamma_1^c &= \ln \left(\frac{3.9243}{0.92} \right) + \frac{10}{2} \times 3.668 \times \ln \left(\frac{3.668 \times 0.92}{1.40 \times 3.9243} \right) \\ &\quad - 1.6428 - \frac{3.9243}{0.92} \times (-2.32) = 0.766 \end{aligned}$$

and from Eq. 11-26

$$\ln \gamma_2^c = 0.0262$$

(4) From Table 11-7

$$a_{1,14} = a_{2,14} = 986.5$$

$$a_{14,1} = a_{14,2} = 156.4$$

$$a_{1,16} = a_{2,16} = 1318$$

$$a_{16,1} = a_{16,2} = 300$$

$$a_{14,16} = 353.5$$

$$a_{16,14} = -229.1$$

$$a_{1,2} = a_{1,1} = a_{2,1} = a_{14,14} = a_{16,16} = 0$$

Using Eq. 11-24

$$\psi_{1,14} = \psi_{2,14} = \exp(-986.5/298) = 0.0365$$

$$\psi_{14,1} = \psi_{14,2} = 0.5917$$

$$\psi_{1,16} = \psi_{2,16} = 0.0120$$

$$\psi_{16,1} = \psi_{16,2} = 0.3654$$

$$\psi_{14,16} = 0.3054$$

$$\psi_{16,14} = 2.157$$

$$\psi_{1,2} = \psi_{1,1} = \psi_{2,1} = \psi_{2,2} = \psi_{14,14} = \psi_{16,16} = 1$$

(5) For pure n-butanol

$$\begin{aligned} X_1^{(1)} &= \frac{\nu_1^{(1)} x_1 + \nu_1^{(2)} x_2}{(\nu_1^{(1)} + \nu_2^{(1)} + \nu_{14}^{(1)} + \nu_{16}^{(1)}) x_1 + (\nu_1^{(2)} + \nu_2^{(2)} + \nu_{14}^{(2)} + \nu_{16}^{(2)}) x_2} \\ &= \frac{1 \times 1 + 0 \times 0}{(1 + 3 + 1 + 0) \times 1 + (0 + 0 + 0 + 0) \times 0} = 1/5 \end{aligned}$$

$$\begin{aligned} X_2^{(1)} &= \frac{\nu_2^{(1)} x_1 + \nu_2^{(2)} x_2}{(\nu_1^{(1)} + \nu_2^{(1)} + \nu_{14}^{(1)} + \nu_{16}^{(1)}) x_1 + (\nu_1^{(2)} + \nu_2^{(2)} + \nu_{14}^{(2)} + \nu_{16}^{(2)}) x_2} \\ &= \frac{3 \times 1 + 0 \times 0}{(1 + 3 + 1 + 0) \times 1 + (0 + 0 + 0 + 0) \times 0} = 3/5 \end{aligned}$$

$$\begin{aligned} X_{14}^{(1)} &= \frac{\nu_{14}^{(1)} x_1 + \nu_{14}^{(2)} x_2}{(\nu_1^{(1)} + \nu_2^{(1)} + \nu_{14}^{(1)} + \nu_{16}^{(1)}) x_1 + (\nu_1^{(2)} + \nu_2^{(2)} + \nu_{14}^{(2)} + \nu_{16}^{(2)}) x_2} \\ &= \frac{1 \times 1 + 0 \times 0}{(1 + 3 + 1 + 0) \times 1 + (0 + 0 + 0 + 0) \times 0} = 1/5 \end{aligned}$$

$$X_{16}^{(1)} = \bar{I}^* - (X_1^{(1)} + X_2^{(1)} + X_{14}^{(1)}) = 0$$

From Eq. set 11-23

$$\Theta_1^{(1)} = \frac{0.848 \times 1/5}{0.848 \times 1/5 + 0.540 \times 3/5 + 1.200 \times 1/5}$$

$$= 0.2312$$

Similarly,

$$\Theta_2^{(1)} = 0.4417$$

$$\Theta_4^{(1)} = 0.3272$$

$$\Theta_6^{(1)} = 0$$

For pure water

$$X_6^{(2)} = 1$$

$$\Theta_6^{(2)} = 1$$

For pure n-butanol, using Eq. 11-22

$$\ln \Gamma_1^{(1)} = Q_1 \left[1 - \ln (\Theta_1^{(1)} \psi_{1,1} + \Theta_2^{(1)} \psi_{2,1} + \Theta_4^{(1)} \psi_{14,1}) \right. \\ \left. - \frac{\Theta_1^{(1)} \psi_{1,1}}{\Theta_1^{(1)} \psi_{1,1} + \Theta_2^{(1)} \psi_{2,1} + \Theta_4^{(1)} \psi_{14,1}} \right. \\ \left. - \frac{\Theta_2^{(1)} \psi_{1,2}}{\Theta_1^{(1)} \psi_{1,2} + \Theta_2^{(1)} \psi_{2,2} + \Theta_4^{(1)} \psi_{14,2}} \right. \\ \left. - \frac{\Theta_4^{(1)} \psi_{1,14}}{\Theta_1^{(1)} \psi_{1,14} + \Theta_2^{(1)} \psi_{2,14} + \Theta_4^{(1)} \psi_{14,14}} \right] \\ = 0.848 \left[1 - \ln (0.2312 + 0.4417 + 0.3272 \times 0.5917) \right. \\ \left. - \frac{0.2312}{0.2312 + 0.4417 + 0.3272 \times 0.5917} \right. \\ \left. - \frac{0.4417}{0.2312 + 0.4417 + 0.3272 \times 0.5917} \right. \\ \left. - \frac{0.3272 \times 0.0315}{(0.2312 + 0.4417) \times 0.0315 + 0.3272} \right] \\ = 0.2859$$

$$\begin{aligned}
\ln \Gamma_2^{(1)} &= Q_2 \left[1 - \ln (\Theta_1^{(1)} \psi_{1,2} + \Theta_2^{(1)} \psi_{2,2} + \Theta_{14}^{(1)} \psi_{14,2}) \right. \\
&\quad - \frac{\Theta_1^{(1)} \psi_{2,1}}{\Theta_1^{(1)} \psi_{1,1} + \Theta_2^{(1)} \psi_{2,1} + \Theta_{14}^{(1)} \psi_{14,1}} \\
&\quad - \frac{\Theta_2^{(1)} \psi_{2,2}}{\Theta_1^{(1)} \psi_{1,2} + \Theta_2^{(1)} \psi_{2,2} + \Theta_{14} \psi_{14,2}} \\
&\quad \left. - \frac{\Theta_{14}^{(1)} \psi_{2,14}}{\Theta_1^{(1)} \psi_{1,14} + \Theta_2^{(1)} \psi_{2,14} + \Theta_{14}^{(1)} \psi_{14,14}} \right] \\
&= 0.540 \left[1 - \ln (0.2312 + 0.4417 + 0.3272 \times 0.5917) \right. \\
&\quad - \frac{0.2312}{0.2312 + 0.4417 + 0.3372 \times 0.5917} \\
&\quad - \frac{0.4417}{0.2312 + 0.4417 + 0.3372 \times 0.5917} \\
&\quad \left. - \frac{0.3272 \times 0.0315}{(0.2312 + 0.4417) \times 0.0315 + 0.3272} \right] \\
&= 0.1821
\end{aligned}$$

$$\begin{aligned}
\ln \Gamma_{14}^{(1)} &= Q_{14} \left[1 - \ln (\Theta_1^{(1)} \psi_{1,14} + \Theta_2^{(1)} \psi_{2,14} + \Theta_{14}^{(1)} \psi_{14,14}) \right. \\
&\quad - \frac{\Theta_1^{(1)} \psi_{14,1}}{\Theta_1^{(1)} \psi_{1,1} + \Theta_2^{(1)} \psi_{2,1} + \Theta_{14}^{(1)} \psi_{14,1}} \\
&\quad - \frac{\Theta_2^{(1)} \psi_{2,14}}{\Theta_1^{(1)} \psi_{1,2} + \Theta_2^{(1)} \psi_{2,2} + \Theta_{14}^{(1)} \psi_{14,2}} \\
&\quad \left. - \frac{\Theta_{14}^{(1)} \psi_{14,14}}{\Theta_1^{(1)} \psi_{1,14} + \Theta_2^{(1)} \psi_{2,14} + \Theta_{14}^{(1)} \psi_{14,14}} \right] \\
&= 1.20 \left\{ 1 - \ln [(0.2312 + 0.4417) \times 0.0315 + 0.3272] \right. \\
&\quad - \frac{0.2312 \times 0.5917}{0.2312 + 0.4417 + 0.3272 \times 0.5917} \\
&\quad \left. - \frac{0.4417 \times 0.0315}{0.2312 + 0.4417 + 0.3272 \times 0.5917} \right\}
\end{aligned}$$

$$- \frac{0.3272}{(0.2312 + 0.4417) \times 0.0315 + 0.3272} \}$$

$$= 1.130$$

For pure water at $x_1 = 0$ (infinitely dilute in n-butanol)

$$\ln \Gamma_6^{(2)} = 0$$

$$\Theta_1 = \Theta_2 = \Theta_{14} = 0$$

$$\Theta_{16} = 1$$

and Eq. 11-22 reduces to

$$\begin{aligned} \ln \Gamma_1 &= Q_1(1 - \ln \psi_{16,1} - \psi_{1,16}) \\ &= 0.848[1 - \ln(0.3654) - 0.0120] \\ &= 1.692 \end{aligned}$$

$$\begin{aligned} \ln \Gamma_2 &= Q_2(1 - \ln \psi_{16,2} - \psi_{2,16}) \\ &= 0.54[1 - \ln(0.3654) - 0.0120] \\ &= 1.077 \end{aligned}$$

$$\begin{aligned} \ln \Gamma_{14} &= Q_{14}(1 - \ln \psi_{16,14} - \psi_{14,16}) \\ &= 1.20[1 - \ln(2.157) - 0.3054] \\ &= -0.0889 \end{aligned}$$

From Eq. set 11-21

$$\begin{aligned} \ln \gamma_1^R &= (1.692 - 0.2859) + 3(1.077 - 0.1821) + (-0.0889 - 1.130) \\ &= 2.871 \end{aligned}$$

and Eq. 11-15

$$\begin{aligned} \ln \gamma_1^\infty &= 0.766 + 2.871 \\ &= 3.637 \\ \gamma_1^\infty &= 38.0 \end{aligned}$$

The experimental value is 52.9 [3] for an error of +28.2%. At $x_1 = 1.0$ (infinitely dilute in water)

$$\begin{aligned} \ln \Gamma_1 &= \ln \Gamma_1^{(1)}; \ln \Gamma_6^{(2)} = 0 \\ \ln \Gamma_2 &= \ln \Gamma_2^{(1)} \end{aligned}$$

$$\ln \Gamma_{14} = \ln \Gamma_4^{(1)}$$

$$\Theta_1 = \Theta_1^{(1)}$$

$$\Theta_2 = \Theta_2^{(2)}$$

$$\Theta_{14} = \Theta_{14}^{(2)}$$

$$\Theta_{16} = 0$$

Using Eq. 11-22

$$\begin{aligned} \ln \Gamma_{16} &= Q_{16} \left[1 - (\Theta_1 \psi_{16,1} + \Theta_2 \psi_{16,2} + \Theta_{14} \psi_{16,14}) \right. \\ &\quad - \frac{\Theta_1 \psi_{1,16}}{\Theta_1 \psi_{1,1} + \Theta_2 \psi_{2,1} + \Theta_{14} \psi_{14,1}} \\ &\quad - \frac{\Theta_2 \psi_{2,16}}{\Theta_1 \psi_{1,2} + \Theta_2 \psi_{2,2} + \Theta_{14} \psi_{14,2}} \\ &\quad \left. - \frac{\Theta_{14} \psi_{14,16}}{\Theta_1 \psi_{1,14} + \Theta_2 \psi_{2,14} + \Theta_{14} \psi_{14,14}} \right] \\ &= 1.4 \left[1 - \ln(0.2312 + 0.4417) \times 0.3654 + 0.3272 \times 2.157 \right. \\ &\quad - \frac{0.2312 \times 0.0120}{0.2312 + 0.4417 + 0.3272 \times 0.5917} \\ &\quad - \frac{0.4417 \times 0.0120}{0.2312 + 0.4417 + 0.3272 \times 0.5917} \\ &\quad \left. - \frac{0.3272 \times 0.3054}{(0.2312 + 0.4417) \times 0.0315 + 0.3272} \right] \\ &= 1.055 \end{aligned}$$

From Eq. set 11-21

$$\ln \gamma_2^R = (1.055 - 0)$$

$$= 1.055$$

$$\ln \gamma_2^\infty = 0.0262 + 1.055$$

$$= 1.081$$

From Eq. 11-15

$$\gamma_2^\infty = 2.95$$

Using Eq. 3-14 of Chapter 3 and the estimated γ_1^∞ , a solubility of 0.026 mole fraction is estimated. This can be compared with an experimental value of 0.018 mole fraction [23].

11-6 AVAILABLE DATA

There are no general compilations of activity coefficients. Infinite dilution activity coefficients for several binary systems are given by Nicolaides [14]. In Reference 8 a fairly extensive list of activity coefficients is given for a variety of binary systems.

11-7 SYMBOLS USED

A	=	parameter in enthalpic equations (Table 11-1)
A_1	=	parameter in Margules equation (Eq. 11-9)
$A_{1,2}$	=	coefficient in Eq. 11-12
a	=	activity in Eq. 11-6
a_{mn}, a_{nm}	=	group interaction parameters
B	=	parameter in enthalpic equations of Table 11-1
B_2	=	coefficient in Eq. 11-12
C	=	parameter in enthalpic equations of Table 11-1
C_1	=	coefficient in Eq. 11-12
D	=	coefficient in Eq. 11-12
F_2	=	coefficient in Eq. 11-12
G^E	=	excess Gibbs free energy (cal)
G^I	=	energy of mixing for an ideal mixture (cal)
G^M	=	energy of mixing in Eq. 11-6 (cal)
G_{21}, G_{12}	=	parameters in NRTL equation, Table 11-1
g^E	=	excess Gibbs free energy per mole (cal/mol)
$\Delta g_{12}, \Delta g_{21}$	=	parameters in NRTL equation, Table 11-1
H	=	Henry's law constant (atm·m ³ /mol)
K_{ow}	=	octanol-water partition coefficient
l_i	=	parameter in UNIQUAC equation (Table 11-1) and Eq. 11-19; $i = 1$ or 2
N_i	=	number of carbon atoms in a molecule in Eq. 11-13; $i = 1$ or 2
N_i', N_i'', N_i'''	=	number of carbon atoms in respective branches of branched compounds; $i = 1$ or 2
n_i	=	number of moles of component i
P_{vp}	=	vapor pressure
P_i°	=	pure component vapor pressure in Eqs. 11-1 to -4; $i = 1$ or 2

P_i	=	partial pressure of component i in Eqs. 11-1 to -4; i = 1 or 2
Q_k	=	van der Waals surface area for group k
q_i	=	molecular van der Waals surface area; i = 1 or 2
R	=	gas constant (1.987 cal/K·mol)
R_k	=	van der Waals volume for group k
r_i	=	molecular van der Waals volume; i = 1 or 2
S	=	solubility (mol/m ³)
S^E	=	excess entropy (e.u.)
T	=	temperature (K)
$\Delta u_{12}, \Delta u_{21}$	=	parameters in UNIQUAC equation (Table 11-1)
X_m	=	group mole fraction for group m
x	=	mole fraction concentration
x_i	=	mole fraction of component i; i = 1 or 2
Z	=	coordination number (set equal to 10)

Greek

α_{12}	=	parameter in NRTL equation (Table 11-1)
Γ_k	=	group activity coefficient
$\Gamma_k^{(j)}$	=	group activity coefficient for pure component j; j = 2 or 1
γ	=	activity coefficient
γ^∞	=	activity coefficient at infinite dilution
γ_i	=	activity coefficient of component i; i = 1 or 2
γ_i^∞	=	activity coefficient of component i at infinite dilution; i = 1 or 2
γ_i^c	=	combinatorial activity coefficient for component i; i = 1 or 2
γ_i^R	=	residual activity coefficient for component i; i = 1 or 2
$(\gamma_W^A)^\infty$	=	infinite dilution activity coefficient of component A in water
$(\gamma_O^A)^\infty$	=	infinite dilution activity coefficient of component A in octanol
$\Lambda_{12}, \Lambda_{21}$	=	parameters in Wilson equation (Table 11-1)
ν_k	=	number of members in group k
$\nu_k^{(j)}$	=	number of members of group k in component j; j = 2 or 1
ϕ_i	=	volume fraction of component i; i = 1 or 2
ψ_{mn}	=	$\exp(-a_{mn}/T)$
ψ_{nm}	=	$\exp(-a_{nm}/T)$

- τ_{ij}, τ_{ji} = parameters in NRTL and UNIQUAC equation
(Table 11-1); $i = 1, 2; j = 2, 1$
- θ_i = molecular surface area fraction ($i = 1$ or 2)
- Θ_m = group surface area fraction

Subscripts

- i = component i
- j = component j
- k = subgroup number
- m = subgroup number
- n = subgroup number
- mn = interaction between groups m and n
- nm = interaction between groups n and m
- o = octanol
- ow = octanol-water
- w = water

Superscripts

- A = component A
- c = combinatorial
- E = excess
- R = residual
- ∞ = infinite

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12

BOILING POINT

Carl E. Rechsteiner, Jr.

12-1 INTRODUCTION

The boiling point is defined [15] as the temperature at which the vapor pressure of a liquid is equal to the pressure of the atmosphere on the liquid. For pure compounds, the normal boiling point is defined [15] as the boiling point at one standard atmosphere of pressure on the liquid. Impurities in the liquid, such as a substance in solution, or pressures other than one atmosphere alter the boiling point of the liquid in a predictable fashion from that of the normal boiling point for the pure substance. A discussion of the factors affecting the boiling point of a compound is presented in §12-10.

Besides being an indicator for the physical state (liquid vs. gas) of a chemical, the boiling point also provides an indication of its volatility. This property is required in most hazard assessment forms and is a needed input for some chemical spill models. Other physical properties, such as critical temperature and enthalpy of vaporization, may be predicted for a pure compound through use of its normal boiling point as one of the input values.

In addition to its utility for predicting physical properties and boiling points at various pressures, the normal boiling point is one of the few parameters known for almost every compound. This is partly because normal boiling points are easily measured: a calibrated thermometer

suspended in a heated vessel containing the pure compound is sufficient, although slightly more elaborate equipment, such as the Cottrell apparatus [4], permits greater accuracy.

This chapter focuses on methods for estimating normal boiling points for organic compounds. Use of this property to predict other physical properties is discussed in the respective chapters of this handbook. The effect of impurities or different pressures on the boiling point is discussed briefly in §12-10.

Estimates of normal boiling points are based on correlations with physical parameters that are influenced by the molecular structures of the compounds. In most instances, correlations are made initially for compounds within a homologous series; these are later extended to a wider range of compounds, if possible.

- Meissner [14] has related the normal boiling points of many classes of organic compounds to their parachors and molar refractions.
- Since the boiling point and the critical temperature are directly related, additive contribution procedures to estimate the critical temperature [3,7,8] and the ratio between the boiling point and the critical temperature [24] may be combined to estimate normal boiling points.
- Forman and Thodos [6,7] use an additive contribution method to compute the van der Waals equation-of-state constants. These constants may be used to find the critical temperature, which, in combination with the boiling point/critical temperature ratio, yields the approximate boiling point.
- The molal liquid volume of an organic compound is another physical parameter that has been correlated with the normal boiling point [16,32].
- Other physical parameters, such as atomic number [25], carbon number [26], and related numbers [2,11,12] have been closely correlated with normal boiling points for very limited groups of compounds.

Molecular connectivity [9,10] is one of a growing family of competitive techniques for predicting boiling points and other physical properties of compounds on the basis of the topology of their atoms. The general procedure is to define one or more parameters whose values depend on

each atom involved and the number of bonds that connect to that atom. Molecular values are computed by summing the individual atomic contributions to the chosen parameters for all of the atoms in the molecule. The molecular values so computed for a series of compounds with known boiling points are then fitted to a regression equation containing a selected number of terms, and that equation is used to estimate the boiling points of similar compounds. A detailed discussion of this and related techniques is not presented here, primarily because most of the regression equations have been reported for aliphatic compounds containing no more than one substituent group, which limits the applicability of this family of techniques. The computation of the individual atomic contributions to the different parameters is also fairly complicated. The other methods presented in this chapter are more amenable to manual calculation.

The methods presented here for the manual estimation of boiling points were developed using sets of fairly simple compounds. To a large extent, the effects of attaching multiple substituent groups to the molecule are assumed to be additive and independent of one another. When estimating boiling points for multifunctional compounds, one should keep in mind that this assumption may not be valid.

12-2 SELECTION OF APPROPRIATE METHOD

Table 12-1 lists recommended methods for estimating normal boiling points, indicates the types of compounds to which each method applies, and lists information concerning input parameters for each method and error specifications from the literature. *None of the estimation methods recommended in this chapter requires any input data beyond the structure of the compound of interest.* This is in contrast to methods in other chapters of this handbook, where knowledge of some related physical properties is essential to the estimation procedures. The methods listed in Table 12-1 are subdivided into two groups according to their range of applicability: the first group comprises the three most broadly useful techniques, and the second group comprises four techniques with limited applications. Detailed descriptions of these methods are presented in the following sections.

For many compounds, more than one method can be used. Table 12-2 compares the estimated boiling points with measured values for some randomly selected compounds. The entries are grouped by compound type and include the absolute and relative errors in terms of

TABLE 12-1

Summary of Methods for Estimating Normal Boiling Points

Sect. No.	Source	Applicability	Basis	Claimed Accuracy
A. Methods with General Application				
12-3	Meissner [14]	Organic compounds containing C, H, N, O, S, and halides. Usable for compounds containing other elements if their molar refraction is measured.	Correlates boiling points with the parachor and the molar refraction of the compound. Adjustment is made for the compound type/class of interest.	Average error of ~2%, maximum error of <8% in K at boiling point.
12-4	Lydersen [24], Forman, Thodos [6,7]	Organic compounds containing C, H, N, O, and halides.	Estimates boiling points from the critical temperature and the ratio between the boiling point and the critical temperature.	Boiling point not expected to be more accurate than 5 to 10 K [24].
12-5	Miller [16]	Most organic compounds.	Estimates boiling points from the boiling point/critical temperature ratio and the critical pressure and critical volume.	
B. Methods with Limited Application				
12-6	Ogata and Tsuchida [20]	Organic compounds containing C, H, N, O, and halides of the form RX, where R is a limited number of hydrocarbon radicals with eight or less carbons.	Estimates boiling points in empirical fashion.	Correlates boiling points for 98% of 600 compounds within 5 K.
12-7	Somayajulu and Palit [25]	Normal alkyl halides, acids, amines, ketones, aldehydes, benzenes, cyclohexanes, and cyclohex-1-enes.	Correlates boiling points with atomic number sum.	Boiling points usually within 5 K
12-8	Kinney [11,12]	Alkanes, alkenes, alkynes, cycloalkanes, and cycloalkenes.	Correlates boiling point with boiling point number.	Boiling point usually within 10 K.
12-9	Stiel and Thodos [26]	Alkanes only.	Correlates boiling point with the number of carbons in saturated aliphatic hydrocarbons.	Average error ~0.5% in K.

TABLE 12-2
Comparison of Boiling Point Estimation Methods for Selected Chemicals
 (All temperatures in K)

A. Hydrocarbons		Known T_b	Meisner [14]		Lydersen [24], Forman, Thodos [6,7]		Miller [16]	
			T_b	Error %	T_b	Error %	T_b	% Error
Methane		109.2	115.9	6.7	6.1	—	121.5	12.3
Butane		272.7	273.4	0.7	0.3	—	281.4	8.7
Isobutane		261.4	277.8	16.4	6.3	0.8	277.3	15.9
Dodecane		489.4	478	-11.4	-2.3	0.4	465.2	-24.2
Cyclohexane		353.9	338.8	-15.1	-4.3	-0.7	358.2	4.3
Ethylene		169.4	172.1	2.7	1.6	-0.1	176.8	7.4
Benzene		353.2	367.2	14	4.0	—	355.6	2.4
m-Xylene		412.2	413.3	1.1	0.3	0.06	405.2	-7.0
Anthracene		613.2	574.4	-38.8	-6.3	-0.3	511.7	-101.5
Chrysene		721.2	652	-69.2	-9.6	0.03	570.0	-151.2
Coronene		798.2	764.3	-33.9	-4.2	-2.0	632.1	-166.1
Avg. Absolute Error			19.1	4.1	22.6	3.0	45.5	8.3

		Ogata and Tsuchida [20]		Somayajulu and Palit [25]		Kinney [11,12]		Stiel and Thodos [26]	
		T_b	Error %	T_b	Error %	T_b	Error %	T_b	% Error
Methane		153.4	44.2	40.5	-0.5	118.1	8.9	126.3	17.1
Butane		264.9	-7.8	-2.9	1.3	273.8	1.1	271.9	-0.8
Isobutane		251.9	-9.5	-3.6	0.7	263.3	1.9	260.4	-1
Dodecane		—	—	—	-0.3	486.9	-2.5	488.1	-1.3
Cyclohexane		—	—	—	—	349.3	-4.6	—	—
Ethylene		178.5	9.1	5.4	—	165.9	-3.5	—	—
Benzene		382	28.8	8.2	—	370.8	17.6	—	—
m-Xylene		—	—	—	—	422.0	9.8	—	—
Avg. Abs. Error		19.9	12.1	1.8	0.7	6.2	2.6	5.0	4.2

(continued)

TABLE 12-2 (Continued)

Known T_b	Meisner [14]		Lydersen [24], Forman, Thodos [6,7]		Miller [16]		Ogata and Tsuchida [20]	
	T_b	Error % Error	T_b	Error % Error	T_b	Error % Error	T_b	Error % Error
B. Sulfur-containing Organics								
Dibutyl sulfide	458.2	-6.6	451.6	-1.4	449.9	-8.3	455.6	-2.6
Diphenyl sulfide	589.2	9.9	578.1	1.7	530.4	-38.8	586.0	26.8
Thiophene	357.3	12.1	368.4	3.4	343.0	-14.3	-	-
Benzothiophene	494.2	4.0	488.2	0.8	459.3	-34.9	-	-
Avg. Absolute Error		8.2		1.8		24.1		14.7
C. Halogen-containing Organics								
2-Fluoronaphthalene	484.6	-19.4	465.2	-4.0	440.3	-44.3		-9.1
1,4-Dichlorobenzene	447.2	-2.3	444.9	-0.5	429.3	-17.9		-4.0
Bromoform	422.6	-6.9	415.7	-1.6	482.1	59.5		14.1
Methylene chloride	313.2	-62	251.2	-19.8	323.1	9.9		3.2
Avg. Absolute Error		22.6		6.5		32.9		7.6
D. Nitrogen-containing Organics								
Aniline	457.3	-28.2	429.1	-6.2	440.2	-17.1	436.6	-20.7
Phenylaniline	575.2	-19	556.2	-3.3	515.8	-59.4		-10.3
Dimethyl amine	280.6	-46.6	234	-16.6	272.9	-7.7	283.2	2.6
Benzonitrile	463.8	-1.0	462.8	-0.2	483.0	19.2	608.1	144.3
Pyridine	388.6	-14.3	374.3	-3.7	452.6	64	400.2	11.6
Indole	527.2	-54.2	473	-10.3	529.7	2.5	454.0	73.2
Benzidine	673.2	-95.3	577.9	-14.2	622.3	-50.9	628.5	-44.7
Acridine	618.6	-36.1	582.5	-5.8	710	91.4	518.0	-100.6
Nitrobenzene	484	-	-	-	462.4	-21.6	464.6	-4.5
Avg. Absolute Error		36.8		7.5		52.8		10.0
							19.2	4.1

(continued)

TABLE 12-2 (Continued)

Known T_b	Meissner [14]		Lydersen [24], Forman, Thodos [6,7]		Miller [16]		Ogata and Tsuchida [20]	
	T_b	Error % Error	T_b	Error % Error	T_b	Error % Error	T_b	Error % Error
E. Oxygen-containing Organics								
Ethanol ^a	351.6	-0.5	345.6	-6	353.8	2.2	346.7	-4.9
Benzyl alcohol	478.5	-7.0	497.5	19	517.6	39.1		-1.4
Benzophenone	579.0	-5.3	584.7	5.7	540.2	-38.8		
Anthraquinone	653.0	-34.1	729.8	76.8	630.6	-22.4		
Dibutyl phthalate	613.2	-9.9	613.6	0.4	598.8	-14.4		
Xanthene	584.2	-15.4	645.1	60.9	510.2	-74.0		
Methyl ethyl ketone	352.8	-2.5	350.4	-2.4	336.2	-16.6	349.4 ^b	-0.4
Furan	304.5	27.8	348.2	43.7	333.8	29.3	353.1	-1.6
Avg. Absolute Error		12.8	26.9	5.5	29.6	6.0		3.2
F. Multifunction/Multihetero- containing Organics								
Chloroethyl vinyl ether	382.2	-14.6	349.7	-32.5	357.9	-24.3		
p-Chloro-m-cresol	508.2	7.5	530.6	22.4	522.5	14.3		
Benzothiazole	504.2	52	-	-	454.3	49.9		
Coumarin	574.9	-122.3	553.6	-21.3	511.9	63.0		
Nicotine	519.2	-15.9	578.6	59.4	485.7	-33.5		
p-Bromo-phenyl isocyanate	431.2	32.3	664.2	233	570.9	139.7		
Nitrosodimethylamine	425.2	-78.8	482.3	57.1	345.8	79.4		
2,4-Thiazolidine-dione	452.2	-28.2	-	-	598.1	145.9		
Avg. Absolute Error		44.0	71.0	15.9	68.8	15.0		

a. The most accurate estimate for ethanol is obtained by the method of Somayajulu and Palit [25], which yields $T_b = 351.4$ K (error = -0.2 K, or -0.06%).
b. Two values of T_b for MEK are obtainable by this method. The error values apply to the average of the two.

percentage difference for each entry. From these tables, several generalizations may be made:

- All of the methods with limited applicability (Table 12-1B) yield estimated boiling points that agree closely with measured values; if these methods are applicable to the compound of interest, they should be used in preference to the more general methods listed in Table 12-1A.
- Of the general methods listed, that of Meissner [14] and that of Lydersen [24] and of Forman and Thodos [6,7] give more accurate boiling point estimates than those computed by the method of Miller [16]. Of the former two, Meissner's method is somewhat easier to compute.
- Because of its lower accuracy, Miller's method should only be used for compounds that cannot be estimated by the two other general methods (e.g., nitro-containing compounds).

12-3 MEISSNER'S METHOD

Principles of Use. The method described by Meissner [14] for estimating normal boiling points is based on their correlation with chemical type; molar refraction, $[R_D]$, and parachor, $[P]$, are used as variables in the correlation. Equation 12-1 relates the normal boiling point, T_b , in K to $[R_D]$, $[P]$ and a constant (B) whose value depends upon the chemical type:

$$T_b = \frac{637 [R_D]^{1.47} + B}{[P]} \quad (12-1)$$

The values for substitution into Eq. 12-1 may be obtained by several methods, as described below.

The molar refraction, $[R_D]$, is defined by

$$[R_D] = \left(\frac{M}{\rho_L} \right) \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \quad (12-2)$$

where M is the molecular weight (g/mole), ρ_L is the liquid density (g/mL), and n_D is the refractive index measured at the wavelength of the sodium D line.¹ All of these values are determined at the same temperature. For

1. Estimation methods for liquid density and refractive index are given in Chapters 19 and 26, respectively.

use in estimating boiling point, however, Eq. 12-2 is of limited utility, since the boiling point is normally determined before either the refractive index or the density is determined.

A simpler method for computing $[R_D]$ is the atomic refraction contribution method of Eisenlohr (referenced in [14]), which consists of summing the contributions for each atom and multiple bond in the compound. These contributions are listed in the second column of Table 12-3.

The parachor, $[P]$, is defined by Sugden's equation (referenced in [14]) as

$$[P] = \frac{M \sigma^{1/4}}{\rho_L - \rho_v} \quad (12-3)$$

where M and ρ_L are as defined above, σ is the surface tension (dynes/cm), and ρ_v is the vapor density (g/mL), all measured at the same temperature.² One may use the method of McGowan [13] to rapidly estimate the parachor for any compound or use the more accurate additive procedure described by Sugden and updated by Mumford and Phillips [18,19].

- *McGowan's method* involves adding contributions for each atom in the compound (see Table 12-4), followed by subtraction of 19 times the number of bonds present in the compound. This method makes no distinction for single or multiple bonds or for differences in contribution due to bonding between different sets of atoms.
- *Sugden's method* adjusts the parachor values for differences in structural features, such as rings and multiple bonds, and for differences caused by bonding between different atom types. The third column of Table 12-3 lists the contributions to be added.

The computation of molar refraction by Eisenlohr's method and parachor by Sugden's method may be simplified through use of Section B of Table 12-3. Since contributions to either term are additive over all of the atoms present in the compound, substructures may be tabulated and used when necessary. For example, the phenyl contribution in monosubstituted benzenes is listed as 25.207 for $[R_D]$ and 190.0 for $[P]$; these values represent the total contributions from 6 carbons, 5 hydrogens, the 6-membered ring, and 3 double bonds.

2. Estimation methods for surface tension and vapor density are given in Chapters 20 and 19, respectively.





TABLE 12-3

Contributions to Molar Refraction and Parachor

Molecular Feature	Molar Refraction, $[R_D]^a$	Parachor, $[P]^b$
A. Atomic Contributions		
C (singly bound)	2.418	9.2
H	1.100	15.4 ^c
O (hydroxyl)	1.525	20
O (in ethers, esters)	1.643	20
O (carbonyl)	2.211 ^d	39 ^d
O ₂ (esters)	3.736	54.8
F	0.95 ^e	25.5
Cl	5.967	55
Br	8.865	69
I	13.900	90
N (primary amine)	2.322	17.5
N (secondary amine)	2.502	17.5
N (tertiary amine or in ring)	2.840	17.5
N (nitrile)	5.516 ^f	55.5 ^f
S	7.690 ^g	50
P	h	40.5
Other elements	h	—
3-member ring	0	12.5
4-member ring	0	6
5-member ring	0	3
6-member ring	0	0.8
7-member ring	0	-4.0
Double bond	1.733	19.0
Semipolar double bond	1.733	0
Triple bond	2.398	38
Singlet linkage	—	-9.5 ⁱ
B. Structural Contributions		
-CH ₂ -	4.618	40.0
-CH ₃	5.718	55.4
-C≡C-	7.234	56.4
-C=C-	6.569	37.4
-C≡N	7.934	64.7

(continued)

TABLE 12-3 (Continued)

Molecular Feature	Molar Refraction, $[R_D]^a$	Parachor, $[P]^b$
B. Structural Contributions (cont'd.)		
	6.154	64.0
	25.207	190.0
	2.625	30.0
	4.629	48.2

- a. $[R_D]$ can be estimated within 5% by this method.
- b. The strain inherent in some kinds of bonds introduces an additional contribution. In the following list of "strain constants," R is a hydrocarbon radical and X is a negative group. (When the negative group is Br, multiply the strain constant by 1.5.)
- Use +3 for carbonyl in the ring.
- Use zero for RCH_2X , $RCHO$, $RCOR$, RCH_2R , RNH_2 , NOR , and $NOOR$.
- Use -3 for $RCHX_2$, $RCOOH$, $RCOOR$, $RCOCl$, R_2CHX , R_2CHR , $RCONH_2$, $ROCOOR$, $ROCOCI$, $RSOOR$, $ROSOOR$, R_2NH , NO_2R , NO_2OR , and azides.
- Use -6 for RCX_3 , R_3CX , RSO_2Cl , R_3CR , RSO_2R , $ROSO_2OR$, R_3N , R_3P , $PO(OR)_3$.
- Use -9 for CX_4 , R_4C .
- c. Hydrogen on oxygen has a parachor of 10; on nitrogen, 12.5; on sulfur and carbon, 15.4.
- d. Includes allowance for double bond.
- e. Only for one fluorine atom attached to carbon; 1.1 for each F in polyfluorides.
- f. Includes allowance for triple bond.
- g. As SH, 7.69; as P, 7.97; as RCNS, 7.91; as RSSR, 8.11.
- h. Value depends on type of compound, apparently differing for various combining forms.
- i. Singlet linkage consists of a bond containing an unpaired electron.

Source: R.H. Perry and C.H. Chilton (eds.), *Chemical Engineers' Handbook*, 5th ed., McGraw-Hill Book Co., New York (1973).

The parameter B is used to adjust the computation of T_b for compound type. Table 12-5 lists values of B for various chemical compound classes. As most of these values were computed from sets of compounds containing only one functional group, this method may not be applicable to compounds containing more than one functional group. However, the tacit assumption is made throughout the development of this method that parachor and molar refraction are additive by either atomic or substructure groupings, and this should extend to the value of B. This

TABLE 12-4

McGowan Parachor Contributions^a

Br	76.1	F	30.5	O	36.2
C	47.6	H	24.7	P	73.5
Cl	62.0	I	98.9	S	67.7
		N	41.9		

a. $[P] = \Sigma (\text{contributions}) - (19) (\text{number of bonds})$

Source: McGowan [13]

TABLE 12-5

Constant B for Various Chemical Classes

Compound Class	B
Acids (monocarboxylic)	28,000
Alcohols (monohydroxy), including phenol, cresols, etc.	16,500
Amines:	
Primary	6,500
Secondary	2,000
Tertiary	-3,000
Esters of monocarboxylic acids with monohydroxy alcohols	15,000
Esters of dibasic acids with monohydroxy alcohols	30,000
Ethers and mercaptans	4,000
Hydrocarbons:	
Acetylenic	-500
Aromatic	-2,500
Paraffinic and naphthenic	-2,500
Olefinic	-4,500
Ketones or aldehydes	15,000
Monochlorinated normal paraffins	4,000
Nitriles	20,000

Source: Meissner [14]

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RESEARCH AND DEVELOPMENT OF METHODS FOR ESTIMATING PHYSICOCHEMICALS ETC(U)

JUN 81 W J LYMAN, W F REEHL, D H ROSENBLATT

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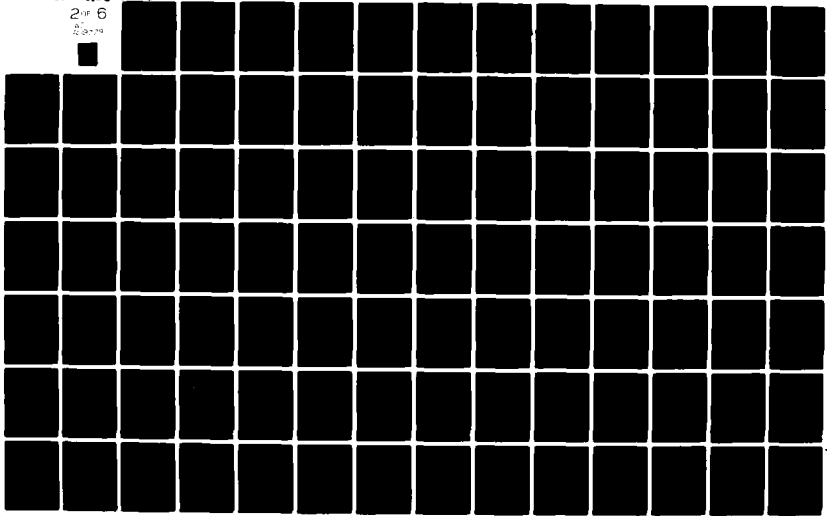
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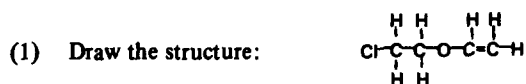
implication is partially borne out by the entries for esters of monocarboxylic acids with monohydroxy alcohols, and for esters of dicarboxylic acids with monohydroxy alcohols. The latter compound class, which has two functional groups, has a value of B twice that of the former class, which has a single functional group. For a number of compounds, including those listed in Table 12-2 which contain multiple functional groups and/or hetero elements, use of a summed value for B (exclusive of the hydrocarbon values) gives estimated boiling points closer to the known values than use of a non-summed B value. (The hydrocarbon values of B are excluded because the data used to develop the B values in Table 12-5 include several types of hydrocarbons, and any hydrocarbon contribution has been averaged into the compound class B values.) It appears that use of a summed B value for complicated molecules will yield more accurate boiling point estimates. If, however, a single value is to be used, the value chosen should be that of the functional group with the largest absolute value, since the larger value indicates that the chemical type has more of an effect on the correlation.

Basic Steps

- (1) Sketch the structure, showing the location of all atoms, rings, and bonds.
- (2) Compute $[R_D]$ by adding the individual atom contributions from Table 12-3A and/or the structural contributions from Table 12-3B. (Additional methods for estimating $[R_D]$ are provided in Chapter 26.)
- (3) Use Sugden's method to find $[P]$, adding the individual atom contributions from Table 12-3A and/or the structural contributions from Table 12-3B. Include strain constants (footnote b) where applicable. Alternatively (McGowan method), add the atom contributions of Table 12-4, then subtract 19 times the number of bonds (whether single, double, or triple). An alternative set of values for structural increments for computing parachor values (Quayle [21]) is provided in Chapter 20 (Table 20-2). Those values include more structural information than the values listed in Table 12-3, and parachor values computed with Quayle's increments tend to be slightly more accurate.
- (4) Determine B for the appropriate chemical type listed in Table 12-5. For multiple hetero functional groups, add the values of B together, excluding any hydrocarbon contribution.

- (5) Compute the normal boiling point from Eq. 12-1 by substituting the derived values of $[R_D]$, $[P]$, and B .

Example 12-1 Estimate the normal boiling point of chloroethyl vinyl ether using Meissner's equation.



- (2) From the molar refraction column of Table 12-3,

4 carbons	=	4(2.418)
7 hydrogens bonded to C	=	7(1.100)
1 oxygen (ether)	=	1(1.643)
1 chlorine	=	1(5.967)
1 double bond	=	<u>1(1.733)</u>
		$[R_D] = 26.715$

- (3) Compute $[P]$:

- By Sugden's method, using Table 12-3,

4 carbons	=	4(9.2)
7 hydrogens	=	7(15.4)
1 oxygen (ether)	=	1(20)
1 chlorine	=	1(55)
1 double bond	=	1(19)
strain	=	<u>---</u>
		$[P] = 238.6$

- By McGowan's method, using Table 12-4,

4 carbons	=	4(47.6)
7 hydrogens	=	7(24.7)
1 oxygen	=	36.2
1 chlorine	=	<u>62.0</u>
		461.5

12 bonds in compound

$$[P] = 461.5 - 19(12)$$

$$= 233.5$$

- (4) From Table 12-5,

Compound has monochlorinated paraffin	$B = 4,000$
Compound has ether	<u>$B = 4,000$</u>
	$\Sigma B = 8,000$

(5) Compute T_b :

- With Sugden's [P] value

$$T_b = \frac{637(26.715)^{1.47} + 8000}{238.6} = 368 \text{ K}$$

$$\text{Error} = -14 \text{ K}$$

- With McGowan's [P] value

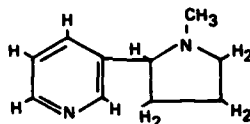
$$T_b = \frac{637(26.715)^{1.47} + 8000}{233.5} = 376 \text{ K}$$

$$\text{Error} = -6 \text{ K}$$

The measured boiling point for chloroethyl vinyl ether is 382.2K; hence this method yields errors of -4% and -2% for boiling points estimated using parachor values computed by the Sugden method and the McGowan method, respectively.

Example 12-2 Estimate the normal boiling point for nicotine.

(1) Draw the structure:



(2) Compute $[R_D]$:

10 carbons	$\approx 10(2.418)$
14 hydrogens bonded to carbon	$\approx 14(1.100)$
2 nitrogen (tert. amine)	$\approx 2(2.840)$
1 6-member ring	≈ 0
1 5-member ring	≈ 0
3 double bonds	$\approx 3(1.733)$

$$[R_D] = 50.459$$

(3) Compute [P] :

- Sugden's method

10 carbons	$\approx 10(9.2)$
14 hydrogens	$\approx 14(15.4)$
2 nitrogens	$\approx 2(17.5)$
1 6-member ring	≈ 0.8
1 5-member ring	≈ 3
3 double bonds	$\approx 3(19)$
strain ³ (2 - R ₃ N)	$\approx 2(-6)$

$$[P] = 391.4$$

3. The aromatic ring in this molecule is considered to contain the R_6N structure in the sense that none of the bonds of the nitrogen atom are connected to a hydrogen atom.

- McGowan's method

$$\begin{array}{rcl} 10 \text{ carbons} & = & 10(47.6) \\ 14 \text{ hydrogens} & = & 14(24.7) \\ 2 \text{ nitrogens} & = & 2(41.9) \\ & & \hline & & 905.6 \end{array}$$

$$[P] = 905.6 - 19(27) = 392.6$$

(4) Compute B:

$$2 \text{ tertiary amines} \quad B = 2(-3,000) = -6,000$$

(5) Compute T_b :

- Sugden's [P] value

$$T_b = \frac{637(50.459)^{1.47} - 6000}{391.4} = 503K$$

$$\text{Error} = -16K$$

- McGowan [P] value

$$T_b = \frac{637(50.459)^{1.47} - 6000}{392.6} = 502K$$

$$\text{Error} = -17K$$

The measured boiling point for nicotine is 519.2K; hence this method yields errors of -3.1% and -3.3% for boiling points estimated using parachor values computed by the Sugden method and the McGowan method, respectively.

12-4 LYDERSEN-FORMAN-THODOS METHOD

Principles of Use. This method is a combination of two separate methods to allow estimation of boiling point. Forman and Thodos [6,7] and Thodos [28,29] have done extensive work on the estimation of critical temperature (T_c) and other critical properties.

Other workers [24] have defined a parameter $\theta = T_b/T_c$ based upon the observation of Guldberg (ref. in [8]) that the ratio is relatively constant for many organic compounds. Accordingly, boiling points can be estimated as follows:

$$T_b = \theta (T_c) \quad (12-4)$$

where θ is the ratio described above.

Calculation of Temperature Ratio, θ . A convenient method of determining θ has been developed by Lydersen [24]. In this method, various ΔT increments relating to the atomic and structural features of the molecule are summed. (See Table 12-6.) $\Sigma \Delta T$ is then substituted into Eq. 12-5 to obtain θ :

$$\theta = 0.567 + \Sigma \Delta T - (\Sigma \Delta T)^2 \quad (12-5)$$

Estimation of Critical Temperature. The estimation of T_c is somewhat more involved. The Forman-Thodos method is based on the following correlation of T_c with van der Waal's constants:

$$T_c = \frac{8a}{27bR} = \frac{0.2963a}{bR} \quad (12-6)$$

where T_c is the critical temperature in K, a and b are van der Waal's constants for the compound, and R is the universal gas constant, expressed as 82.05 atm-cm³/mol-K. The constants a and b are related to structure and can be estimated by summing the appropriate increments. One complication is that the additive structural increments contribute to the appropriate van der Waal's constant raised to a power rather than directly to the van der Waal's constant. In the original correlations, the exponents had the values of 0.626 for a and 0.76 for b , which were later rounded to 2/3 and 3/4. The tables included here list the increments in terms of $a^{2/3}$ and $b^{3/4}$; thus, before the critical temperature is computed from Eq. 12-6, the sum of the additive terms must be raised to the appropriate power (3/2 for a , and 4/3 for b).

To use this method, each molecule is considered to be an aggregate of various types of carbon atoms and functional groups; -OH, -NO₂, -CO₂H are examples of functional groups. Hydrogen atoms are not considered, except for their role in defining carbon atom types or functional group types. The contributions to $a^{2/3}$ and $b^{3/4}$ are summed for each carbon type present in the molecule, adjusted for the presence of rings and multiple bonds, and finally added to the contributions of the other functional groups in the molecule. Figure 12-1 shows the carbon types used with this method. The type number refers to the number of bonds between the central carbon atom and other carbon atoms or functional groups. Letters following some type numbers indicate their use in the compound, i.e., in aliphatics, in olefins, in cyclo- or naphthenic compounds, and in aromatics with or without fused rings. The following paragraphs explain how contributions for different carbon types are computed.

TABLE 12-6

Lydersen's Increments for Calculating $\Sigma\Delta T$

- There are no increments for hydrogen.
- All bonds shown as free are connected to atoms other than H.
- Values in parentheses are based upon too few experimental values to be reliable [24].

Increment	ΔT	Increment	ΔT
Nonring increments:		Oxygen increments:	
$-\text{CH}_3$	0.020	$-\text{OH}$ (alcohols)	0.082
$-\text{CH}_2$	0.020	$-\text{OH}$ (phenols)	0.031
$-\text{CH}$	0.012	$-\text{O}-$ (nonring)	0.021
$-\text{C}-$	0	$-\text{O}-$ (ring)	(0.014)
$=\text{CH}_2$	0.018	$-\text{C}=\text{O}$ (nonring)	0.040
$=\text{CH}$	0.018	$-\text{C}=\text{O}$ (ring)	(0.033)
$=\text{C}-$	0	$\text{HC}=\text{O}$ (aldehyde)	0.048
$=\text{C}=\text{}$	0	$-\text{COOH}$ (acid)	0.085
$\equiv\text{CH}$	0.005	$-\text{COO}-$ (ester)	0.047
$\equiv\text{C}-$	0.005	$=\text{O}$ (exc. for above combinations)	(0.02)
Ring increments:		Nitrogen increments:	
$-\text{CH}_2-$	0.013	$-\text{NH}_2$	0.031
$-\text{CH}$	0.012	$-\text{NH}$ (nonring)	0.031
$-\text{C}-$	(-0.007)	$-\text{NH}$ (ring)	(0.024)
$=\text{CH}$	0.011	$-\text{N}-$ (nonring)	0.014
$=\text{C}-$	0.011	$-\text{N}-$ (ring)	(0.007)
$=\text{C}=\text{}$	0.011	$-\text{CN}$	(0.060)
$\text{C}-\text{H}$ (common to 2 saturated condensed rings)	0.064	$-\text{NO}_2$	(0.055)
Halogen increments:		Sulfur increments:	
$-\text{F}$	0.018	$-\text{SH}$	0.015
$-\text{Cl}$	0.017	$-\text{S}-$ (nonring)	0.015
$-\text{Br}$	0.010	$-\text{S}-$ (ring)	(0.008)
$-\text{I}$	0.012	$=\text{S}$	(0.003)

Source: Reid and Sherwood [24]

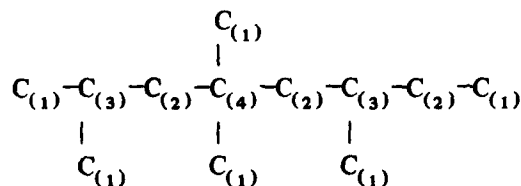
ALIPHATIC			
$\begin{array}{c} \text{H} \\ \\ -\text{C}-\text{H} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \\ -\text{C}-\text{H} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \\ -\text{C}-\text{H} \\ \end{array}$	$\begin{array}{c} \\ -\text{C}- \\ \end{array}$
Type 1	Type 2	Type 3	Type 4
OLEFINIC			
$\begin{array}{c} \\ =\text{C}-\text{H} \end{array}$			
Type 3u			
NAPHTHENIC (in-ring)			
$\begin{array}{c} \text{H} \\ \\ \diagup \text{C} \diagdown \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \diagup \text{C} \diagdown \\ \end{array}$	$\begin{array}{c} \\ \diagup \text{C} \diagdown \\ \end{array}$	
Type 2n	Type 3n	Type 4n	
AROMATIC			
$\begin{array}{c} \diagup \\ \text{C}-\text{H} \\ \end{array}$	$\begin{array}{c} \diagup \\ \text{C}- \\ \end{array}$	$\begin{array}{c} \text{C} \\ \diagup \\ \text{C} \\ \end{array}$	
Type 3a	Type 4a	Type 4p (fused ring)	

Source: Forman and Thodos [6].

FIGURE 12-1 Carbon Types Used in Forman-Thodos Estimation of Critical Temperature

Individual contributions to $a^{2/3}$ and $b^{3/4}$ will be referred to as $\Delta a^{2/3}$ and $\Delta b^{3/4}$. These contributions depend on both the carbon type and the number of carbon atoms plus functional atoms.

• *Contributions for Carbon Types.* Table 12-7 lists the specific values for the different carbon types for $2 \leq n \leq 15$, where n is the total number of carbon atoms and functional atoms. Table 12-8 lists the regression equations from which the specific values in Table 12-7 originate. In the following example, which shows only the carbon skeleton, the molecule contains six type 1 carbons (-C), three type 2 carbons (-C-), two type 3 carbons (-C-), and one type 4 carbon (-C-). (The parenthetical subscripts are the type numbers.)



As this compound contains 12 carbon atoms and no functional atoms, $n = 12$.

• *Corrections for Branching.* An adjustment is made to the summed $\Delta a^{2/3}$ and $\Delta b^{3/4}$ terms if any branching is found in the hydrocarbon (i.e., if any type 3 or type 4 carbon atoms are present). The correction that is made is:

$$\Sigma \Delta a^{2/3} \text{ (correct)} = f_a \Sigma \Delta a^{2/3} \text{ (computed)} \quad (12-7)$$

$$\Sigma \Delta b^{3/4} \text{ (correct)} = f_b \Sigma \Delta b^{3/4} \text{ (computed)} \quad (12-8)$$

$$f_a = (1/3) [(W_i/W_n) + 2 + 0.087 m + 0.0045 \sum_{k=1}^m k(k-1)] \quad (12-9)$$

$$f_b = (1/2) [(W_i/W_n + 1 + 0.101 m - 0.005 m^2)] \quad (12-10)$$

m = total number of side chains attached to the main (longest) carbon chain

W = Wiener number

TABLE 12-7

Group Contributions $\Delta_a^{2/3}$ and $\Delta_b^{3/4}$ for
Saturated Aliphatic Hydrocarbons

n ^a	$\begin{array}{c} \text{H} \\ \\ -\text{CH} \text{ Type 1} \\ \\ \text{H} \end{array}$		$\begin{array}{c} \\ -\text{CH} \text{ Type 2} \\ \\ \text{H} \end{array}$		$\begin{array}{c} \\ -\text{C}-\text{H} \text{ Type 3} \\ \end{array}$		$\begin{array}{c} \diagup \diagdown \\ \text{C} \text{ Type 4} \end{array}$	
	$\Delta_a^{2/3}$	$\Delta_b^{3/4}$	$\Delta_a^{2/3}$	$\Delta_b^{3/4}$	$\Delta_a^{2/3}$	$\Delta_b^{3/4}$	$\Delta_a^{2/3}$	$\Delta_b^{3/4}$
1								
2	15,577	11.453						
3	15,216	11.453	13,678	6.262				
4	15,035	11.453	13,678	6.262	12,567	2.064		
5	14,927	11.453	13,678	6.262	11 189	0.886	6,181	-4.937
6	14,854	11.453	13,678	6.282	10,270	0.101	4,980	-6.670
7	14,803	11.453	13,678	6.262	9,614	-0.460	4,123	-7.909
8	14,764	11.453	13,678	6.262	9,122	-0.880	3,480	-8.837
9	14,734	11.453	13,678	6.262	8,739	-1.207	2,979	-9.559
10	14,710	11.453	13,678	6.262	8,433	-1.469	2,579	-10.337
11	14,690	11.453	13,678	6.262	8,182	-1.683	2,252	-10.160
12	14,674	11.453	13,678	6.262	7,974	-1.862	1,979	-11.004
13	14,660	11.453	13,678	6.262	7,797	-2.012	1,748	-11.337
14	14,648	11.453	13,678	6.262	7,646	-2.142	1,550	-11.623
15	14,638	11.453	13,678	6.262	7,514	-2.254	1,379	-11.870

a. n = total number of carbon atoms and functional atoms.

Source: Forman and Thodos [6]

TABLE 12-8

Equations for $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for Saturated Aliphatic Hydrocarbons Containing n Carbons ($2 < n < 15$)

Type	$\Delta a^{2/3}$	$\Delta b^{3/4}$
1 $\begin{array}{c} \text{H} \\ \\ -\text{C}-\text{H} \\ \\ \text{H} \end{array}$	$= (2,168/n) + 14,493$	$= \text{constant} = 11.453$
2 $\begin{array}{c} \\ -\text{C}-\text{H} \\ \\ \text{H} \end{array}$	$= \text{constant} = 13,678$	$= \text{constant} = 6.262$
3 $\begin{array}{c} \\ -\text{C}-\text{H} \\ \end{array}$	$= (27,560/n) + 5,677$	$= (23.55/n) - 3.824$
4 $\begin{array}{c} \\ -\text{C}- \\ \end{array}$	$= (36,013/n) - 1,022$	$= (52.00/n) - 15.337$

Source: Foreman and Thodos [6]

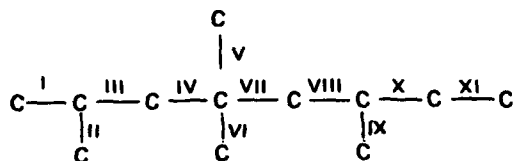
The subscripts i and n refer to the isomer of interest and to the corresponding normal alkane respectively. To compute the Wiener number, the number of carbons on the two sides of any bond are multiplied together and summed for all of the carbon-to-carbon bonds. For convenience, the Wiener number for the normal alkane can be computed from Eq. 12-11.

$$W_n = \frac{(N-1)(N)(N+1)}{6} \quad (12-11)$$

where N is the number of carbon atoms in the hydrocarbon.

Example 12-3 illustrates the computation of $a^{2/3}$, $b^{3/4}$, and Wiener numbers for the compound shown previously.

Example 12-3 Compute $a^{2/3}$ and $b^{3/4}$ using the Forman-Thodos method for 2,4,4,6-tetramethyl octane, whose carbon skeleton is shown below. (The bonds are individually numbered for reference.)



(1) Calculate $\Delta a^{2/3}$ and $\Delta b^{3/4}$ values

- Total number of carbons = 12
- From Table 12-7

	$\Delta a^{2/3}$	$\Delta b^{3/4}$
six type 1 carbons	6(14,674)	6(11.453)
three type 2 carbons	3(13,678)	3(6.262)
two type 3 carbons	2(7,974)	2(-1.862)
one type 4 carbon	1(1,979)	1(-11.004)
	$\Sigma \Delta a^{2/3} = 147,005$	$\Sigma \Delta b^{3/4} = 72.776$

(2) Compute correction factors

- Total number of side chains (m) = 4
- From Eq. 12-11

$$W_n = \frac{(12-1)(12)(12+1)}{6}$$

$$= 286$$

- Compute W_i as follows:

For bond	I:	$1 \times 11 = 11$
	II:	$1 \times 11 = 11$
	III:	$3 \times 9 = 27$
	IV:	$4 \times 8 = 32$
	V:	$1 \times 11 = 11$
	VI:	$1 \times 11 = 11$
	VII:	$7 \times 5 = 35$
	VIII:	$8 \times 4 = 32$
	IX:	$11 \times 1 = 11$
	X:	$10 \times 2 = 20$
	XI:	$11 \times 1 = 11$
	W_i	$= 212$

- From Eq. 12-9

$$\begin{aligned} f_a &= (1/3)[(212/286) + 2 + 0.087(4) + 0.0045 \sum_{k=1}^4 k(k-1)] \\ &= (1/3)[0.7413 + 2 + 0.348 + 0.0045(20)] \\ &= 1.060 \end{aligned}$$

- $$\begin{aligned} f_b &= (1/2)[(212/286) + 1 + 0.101(4) - 0.005(4)^2] \\ &= (1/2)[0.7413 + 1 + 0.404 - 0.080] \\ &= 1.033 \end{aligned}$$

- (3) Correct $\Delta a^{2/3}$ and $\Delta b^{3/4}$ using Eqs. 12-7 and 12-8.

- $\Delta a^{2/3}(\text{correct}) = 1.060(147,005) = 155,800$
- $\Delta b^{3/4}(\text{correct}) = 1.033(72,776) = 75.18$

• *Contributions for Multiple Bonds.* For compounds containing multiple bonds, an initial computation of $\Delta a^{2/3}$ and $\Delta b^{3/4}$ is made using the saturated analog of the compound of interest. The multiple bonds are then inserted in the proper location, and appropriate contributions are added to $\Delta a^{2/3}$ and $\Delta b^{3/4}$. Table 12-9 lists the contributions due to unsaturation for various carbon atom types. For a single unsaturated bond, the contribution is found directly from the table using the type numbers shown in Figure 12-1 for the two carbon atoms involved in the saturated bond. Returning to Example 12-3, assume that we wish to make bond III a double bond; the two carbon atoms involved are types 3 and 2, so the contribution for a 3-2 double bond should be used. If we wish to make bond XI a triple bond, the two carbon atoms involved are types 1 and 3, so the contribution for a 3-1 triple bond should be used.

The introduction of more than one double bond alters the contributions that are used for the type 3 carbons and those for a bond that extends the conjugation of the molecule. (Conjugation occurs when there is more than one double bond in a molecule and the double bonds are separated from one another by a single bond.) The carbons joined by double bonds become type 3u, illustrated in Figure 12-1. If an additional double bond joins one of these carbons to another carbon of some type n, a contribution must be incorporated in the $\Delta a^{2/3}$ and $\Delta b^{3/4}$ terms for the 3u-to-n bond. For type 3 carbons, the appropriate contribution from Table 12-9B is used. If the additional double bond is conjugated with a

TABLE 12-9

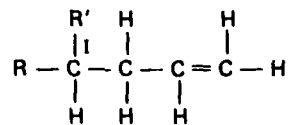
Double- and Triple-Bond Contributions
in Forman and Thodos Method

	$\Delta a^{2/3}$	$\Delta b^{3/4}$
A. First double bond		
(1-1)	-3,868	-2.021
(2-1)	-3,154	-1.895
(2-2)	-2,551	-2.009
(3-1)	-1,548	-1.706
(3-2)	- 928	-1.820
(3-3)	- 540	-1.930
B. Second double bond		
(3-1)	- 828	-1.259
(3-2)	- 496	-1.343
(3u-1)	-1,332	-1.745
(3u-2)	-1,324	-1.862
(3u-3)	-1,316	-1.979
(3u \leftarrow 2-1)	-1,687	-1.399
(3u \leftarrow 2-2)	- 910	-1.485
C. Triple bond		
(1-1)	-4,269	-3.680
(2-1)	-1,934	-3.008
(2-2)	-1,331	-3.122

Source: Forman and Thodos [6]

type 3u carbon (i.e., there is an intervening type 2 carbon), the contributions to the $\Delta a^{2/3}$ and $\Delta b^{3/4}$ terms must reflect the conjugation in the molecule.

An example may help to clarify the multiple-double-bond calculation.

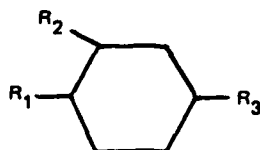


In this partial structure, if R and R' are both hydrogens (i.e., the associated carbon is a type 1), the contributions to $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for a double bond inserted at location I would be for a $3u \leftarrow 2-1$ double bond, where the arrow indicates conjugation through the type 2 carbon. If R is a hydrocarbon radical and R' is hydrogen (type 2 carbon), the contributions for a double bond at I would be for a $3u \leftarrow 2-2$ double bond. If both R and R' are hydrocarbon radicals (type 3 carbon), the contributions for a double bond at location I would be for a 3-2 double bond. For other bond locations where an additional double bond is neither conjugated to a previous double bond nor involves a type 3 carbon, the contributions to $\Delta a^{2/3}$ and $\Delta b^{3/4}$ are the same as if the added double bond were the only double bond in the molecule. (Use Table 12-9A.)

• *Naphthenic Compounds.* The contributions for atoms in the rings of naphthenic compounds (cycloalkanes) are different from those for carbons in alkyl sidechains, and an additional contribution is attributable to the ring structure per se. The values for carbon types 2n, 3n, and 4n are listed in Table 12-10 along with the naphthene ring contribution.

For multiple naphthene rings in a compound, a contribution to $\Delta a^{2/3}$ and $\Delta b^{3/4}$ is made for each ring. If the cycloalkane has more than one substituent in the ring, the additional strain on the ring is reflected in positional contributions which vary for *cis* and *trans* configurations; these are also listed in Table 12-10.

In their original work, Forman and Thodos [6] and Thodos [25] obtained data only for 1,2 and 1,3 disubstitutions. For other disubstitutions such as 1,4 or 1,1, they recommended that the contribution for a 1,3 disubstitution be used. While neither author dealt with tri-, tetra-, etc. substitutions, they suggested that the disubstitution rules be used sequentially to account for all of the substitutions. As an example, consider the following tri-substituted cyclohexane:



This compound would have a (1,2) disubstitution for the pair R_1R_2 , a (1,3) disubstitution for the pair R_1R_3 , and a (1,4) disubstitution for the pair R_2R_3 . The contribution for the last disubstitution would be taken from the appropriate (1,3) disubstitution entry of Table 12-10. In general, a trisubstituted molecule would have three disubstitution contributions, etc.

TABLE 12-10

Naphthenic and Aromatic Contributions
in Forman and Thodos Method

	$\Delta a^{2/3}$	$\Delta b^{3/4}$
Carbon Type		
2n	12,535	5.338
3n	9,910	0.023
4n	2,066	-8.094
3a	11,646	5.991
4a	11,144	1.043
4p	11,561	1.634
Naphthenic ring contribution	2,658	9.073
Aromatic ring contribution	0	0
Position contribution from multiple substitution:		
Naphthene rings		
cis-1,2	- 427	-0.866
1,3	- 2,525	-1.493
trans-1,2	- 2,525	-1.493
1,3	- 4,195	-2.494
Aromatic rings		
1-2	- 830	-1.253
1-3	- 1,597	-0.806
1-4	155	0.212
1-5	279	0.254
1-6	488	0.525

Source: Adapted from Thodos [28,29]

• *Aromatic Compounds.* Aromatic compounds are handled in the same way as cycloalkanes. The three types of aromatic carbons shown in Figure 12-1 are used to account for isolated aromatic rings (types 3a and 4a) and fused rings (type 4p). Their contributions are listed in Table 12-10. There is no additional contribution for the aromatic structure. Multiple substitutions to aromatic rings are accounted for in the same fashion as were multiple substitutions to naphthene rings.

• *Functional Groups.* The final contributions to the $\Delta a^{2/3}$ and $\Delta b^{3/4}$ terms are due to any functional groups present. These contributions

depend on the functional group involved and the number of carbon and functional atoms present, according to Eqs. 12-12 and 12-13:

$$\Delta a^{2/3} = K_1/n + K_2 \quad (12-12)$$

$$\Delta b^{3/4} = K_3/n + K_4 \quad (12-13)$$







Values for K_1 , K_2 , K_3 , and K_4 are listed in Table 12-11, and n is the total number of carbon atoms and functional group atoms. Halogens attached to a single carbon in aliphatic compounds have different contributions to $\Delta a^{2/3}$ and $\Delta b^{3/4}$, depending on the number of halogen atoms attached to that carbon. The procedure for assigning halogen contributions is to use the lower weight halogens first and find their contribution in Table 12-11. For example, in fluorodichloromethane, there would be a "first fluoride" contribution, a "second chloride" contribution, and a "third chloride" contribution to account for the halogens.

Basic Steps

- (1) Sketch the molecule, showing the location of the atoms, rings, and double bonds.
- (2) Compute ΔT by summing atom contributions from Table 12-6.
- (3) Compute θ using Eq. 12-5.
- (4) For aliphatic portion(s) of the molecule, sketch completely saturated side chains.
- (5) Compute aliphatic contributions to $\Delta a^{2/3}$ and $\Delta b^{3/4}$ using Table 12-7 and Eqs. 12-7 to 12-11.
- (6) Compute contribution to $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for any sites of unsaturation using Table 12-9.
- (7) Compute contributions to $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for any naphthene and aromatic rings using Table 12-10.
- (8) Compute contributions to $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for any functional groups using Table 12-11 and Eqs. 12-12 and 12-13.
- (9) Sum contributions to $\Delta a^{2/3}$ and $\Delta b^{3/4}$.
- (10) Compute a and b by $(\sum \Delta a^{2/3})^{3/2}$ and $(\sum \Delta b^{3/4})^{4/3}$.
- (11) Compute T_c from Eq. 12-6.
- (12) Compute T_b from Eq. 12-4.

TABLE 12-11

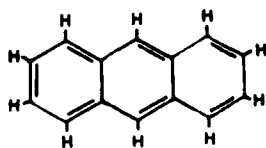
Constants for Equations that Establish Functional Group Contributions
for Organic Compounds in Forman and Thodos Methods

	Functional Group	$\Delta_a^{2/3} = K_1/n + K_2$		$\Delta_b^{3/4} = K_3/n + K_4$	
		K_1	K_2	K_3	K_4
Alcohols	-OH	30,200	14,000	8.96	7.50
Phenols	-OH	0	8,500	0	4.19
Ethers:					
nonycyclic	-O-	14,500	6,500	0	3.26
cyclic	-O-	0	9,440	0	2.74
Ketones		62,800	16,700	27.20	4.55
Carboxylic acids		142,670	16,730	66.80	5.10
Acid anhydrides		0	43,880	0	14.78
Esters:					
Formates	HCO-	35,140	26,800	2.29	15.80
Others		37,430	25,500	- 3.00	12.00
Amines:					
Primary	-NH ₂	4,800	18,900	0	10.15
Secondary		51,800	0	19.60	- 1.10
Tertiary		60,200	- 4,300	29.20	- 7.90
Nitriles	-CN	86,000	25,900	39.70	12.10
Aliphatic halides:					
Fluorides	-F				
First		2,420	12,240	- 3.70	10.92
Second		-38,500	4,510	-48.50	12.86
Third		0	3,450	0	6.92
Chlorides	-Cl				
First		0	22,580	0	11.54
Second		66,000	- 5,100	19.00	3.90
Third		-60,250	29,100	-40.80	19.40
Fourth		0	16,500	0	11.46
Bromides	-Br				
First		- 2,720	23,550	- 4.35	11.49
Second		0	20,860	0	5.37
Iodides	-I				
First		0	33,590	0	13.91
Aromatic halides:					
Fluoride	-F	0	4,210	0	7.22
Chloride	-Cl	0	17,200	0	10.88
Bromide	-Br	0	24,150	0	12.74
Iodide	-I	0	34,780	0	15.22

Source: Forman and Thodos [7]

Example 12-4 Compute the normal boiling point for anthracene by the Lydersen-Forman-Thodos method.

- (1) Sketch anthracene



- (2) From Table 12-6:

$$10(\overset{|}{=}\text{CH ring}) = 10(.011)$$

$$4(=\text{C} \diagdown \text{ring}) = \underline{4(.011)}$$

$$\Sigma \Delta T = 0.154$$

- (3) From Eq. 12-5:

$$\theta = 0.567 + (0.154) - (0.154)^2$$

$$= 0.697$$

- (4) The only contributions to a and b in this compound are for the carbons in the aromatic rings. From Table 12-10,

	$\frac{\Delta a^{2/3}}$	$\frac{\Delta b^{3/4}}$
10 [=C-H ring, type 3a]	= 10(11,646)	10(5.991)
4 [=C- ring, type 4P]	= <u>4(11,561)</u>	<u>4(1.634)</u>
Σ	= 162,704	66.446

(5) $a = (162,704)^{3/2} = 65,629,000$

$$b = (66.446)^{4/3} = 269.138$$

- (6) From Eq. 12-6,

$$T_c = \frac{(8)(65,629,000)}{(27)(269.13)(82.05)}$$

$$= 880.6$$

- (7) From Eq. 12-4,

$$T_b = \theta T_c$$

$$= (0.697)(880.6)$$

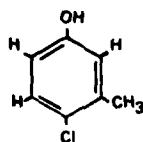
$$= 614$$

Error = 1K

The measured boiling point for anthracene is 613.2K; thus, this method shows a relative error of 0.2%.

Example 12-5 Compute the normal boiling point for p-chloro-m-cresol by the Lydersen-Forman-Thodos method.

- (1) Sketch molecule



- (2) From Table 12-6:

$$\begin{aligned}
 -\text{OH} &= 0.031 \\
 -\text{CH}_3 &= 0.020 \\
 -\text{Cl} &= 0.017 \\
 3 \text{ (}=\text{CH ring)} &= 3 (0.011) \\
 3 \text{ (}=\text{C}^{\text{I}}\text{ ring)} &= 3 (0.011) \\
 \Sigma \Delta T &= 0.134
 \end{aligned}$$

- (3) From Eq. 12-5:

$$\begin{aligned}
 \theta &= 0.567 + 0.134 - (0.134)^2 \\
 &= 0.683
 \end{aligned}$$

- (4) The "aliphatic side chain" ($-\text{CH}_3$) contains a type 1 carbon, and the total number of carbon and functional group atoms, $n = 7 \text{ (C)} + 1 \text{ (Cl)} + 1 \text{ (O)} = 9$. Therefore, from Table 12-7, the aliphatic contributions to a and b are

$$\Delta a^{2/3} = 14,734$$

$$\Delta b^{3/4} = 11.453$$

- (5) The contributions for the aromatic ring (Table 12-10) are:

	$\Delta a^{2/3}$	$\Delta b^{3/4}$
3 (type 3a)	3 (11,646)	3 (5,991)
3 (type 4a)	3 (11,144)	3 (1,043)
Ring	0	0

Multiple substitutions⁴

(1-3)	-1,597	-0.806
(1-2)	-830	-1.253
(1-4)	<u>155</u>	<u>0.212</u>
	$\Delta a^{2/3} = 66,098$	$\Delta b^{3/4} = 19.255$

- (6) Obtain the functional group contributions from Table 12-11.

For -OH (phenol) $K_1 = 0$, $K_2 = 8,500$, $K_3 = 0$, $K_4 = 4.19$

By Eq. 12-12, $\Delta a^{2/3} = 0/9 + 8,500 = 8,500$

By Eq. 12-13, $\Delta b^{3/4} = 0/9 + 4.19 = 4.19$

For -Cl (aromatic) $K_1 = 0$, $K_2 = 17,200$, $K_3 = 0$, $K_4 = 10.88$

$\Delta a^{2/3} = 0/9 + 17,200 = 17,200$

$\Delta b^{3/4} = 0/9 + 10.88 = 10.88$

- (7) Totaling the contributions from steps 4, 5, and 6:

$\Delta a^{2/3} = 14,734 + 66,098 + 8,500 + 17,200 = 106,532$

$\Delta b^{3/4} = 11.453 + 19.255 + 4.190 + 10.880 = 45.778$

- (8) $a = (106,532)^{3/2} = 34,771,000$

$b = (45.778)^{4/3} = 163.76$

- (9) From Eq. 12-6,

$$T_c = \frac{(8) (34,771,000)}{(27) (163.76) (82.05)} = 766.8$$

- (10) From Eq. 12-4,

$$T_b = (0.683) (766.8) = 524K$$

Error = 16K

The measured boiling point for p-chloro-m-cresol is 508.2K; thus, this method shows an error of 3.1%.

4. Recall that the substitution notation describes the relationship between a given substitution and the one that precedes it in a counterclockwise direction. Thus, although CH₃ and Cl are in ring positions 3 and 4 respectively, the Cl is considered a 1-2 substitution in the Forman and Thodos method, because its reference is the CH₃ radical.

12-5 MILLER'S METHOD

Miller [16] combined the empirical work of Rackett [22] and that of Tyn and Calus [30] to produce a method of estimating the normal boiling point of any organic compound from its critical properties — P_c , the critical pressure, V_c , the critical volume, and θ , the ratio of the normal boiling point, T_b , to the critical temperature, T_c . The three required parameters for this method, P_c , V_c , and θ , may be estimated via the techniques of Lydersen [24].

Tyn and Calus proposed Eq. 12-14 to relate the molal liquid volume at the normal boiling point, V_b , to the critical volume, V_c , where both volumes are expressed in terms of cm^3 per mole.

$$V_b = 0.285 V_c^{1.048} \quad (12-14)$$

Rackett developed an empirical equation to relate the reduced volume of saturated liquids to the critical compressibility factor and the reduced temperature. At the normal boiling point, the Rackett equation becomes

$$V_b = \left(\frac{RT_c}{P_c} \right) Z_c^{1.0 + (1.0 - \theta)^{2/7}} \quad (12-15)$$

where V_b is the molal liquid volume at the normal boiling point, T_c is the critical temperature in K, P_c is the critical pressure in atm, Z_c is the critical compressibility factor, θ is the ratio of T_b/T_c , and R is the universal gas constant with a value of $82.054 \text{ cm}^3\text{-atm/mol K}$. On combining Eqs. 12-14 and 12-15 and solving for T_c , one obtains:

$$T_c = \frac{e^\beta}{R} \quad (12-16)$$

where

$$\beta = \frac{[(1 - \theta)^{2/7} - 0.048] \ln(V_c) + [1 - \theta]^{2/7} \ln(P_c) + 1.255}{[1 - \theta]^{2/7}} \quad (12-17)$$

The normal boiling point may then be computed from Eq. 12-4.

In §12-4, the Lydersen method for estimating θ was presented. Lydersen has developed analogous methods for estimating P_c and V_c .

Pressure increments (or volume increments) are summed for each atomic and structural feature of the molecule. The increment sums found in Table 12-12 are substituted into Eq. 12-18 or 12-19 to compute the critical pressure or the critical volume, respectively.

$$P_c = \frac{M}{(0.34 + \Sigma\Delta P)^2} \quad (12-18)$$

and

$$V_c = 40 + \Sigma\Delta V \quad (12-19)$$

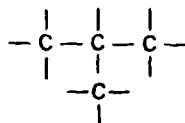
where M is the molecular weight in grams per mole.

Basic Steps

- (1) Sketch the structure, showing the location of all atoms, rings, and bonds.
- (2) Find $\Sigma\Delta T$, $\Sigma\Delta P$, and $\Sigma\Delta V$ by summing the appropriate increments in Tables 12-6 and 12-12.
- (3) Compute θ using Eq. 12-5.
- (4) Compute P_c using Eq. 12-18.
- (5) Compute V_c using Eq. 12-19.
- (6) Compute β using 12-17.
- (7) Compute T_b from Eqs. 12-16 and 12-4.

Example 12-6 Estimate the normal boiling point of isobutane (molecular weight = 58.13).

- (1) Sketch isobutane:



- (2) Find $\Sigma\Delta T$, $\Sigma\Delta P$, and $\Sigma\Delta V$ from Tables 12-6 and 12-12.

	ΔT	ΔP	ΔV
3(-CH ₃)	3(0.020)	3(0.227)	3(55)
1(-CH)	0.012	0.210	51
	$\Sigma\Delta T = 0.072$	$\Sigma\Delta P = 0.891$	$\Sigma\Delta V = 216$

TABLE 12-12

Lydersen's Increments for Calculating $\Sigma\Delta P$ and $\Sigma\Delta V^{a,b,c}$

Increment	ΔP	ΔV
Nonring increments		
$-\text{CH}_3$	0.227	55
$-\text{CH}_2-$	0.227	55
$-\text{CH}-$	0.210	51
$-\text{C}-$	0.210	41
$=\text{CH}_2$	0.198	45
$=\text{CH}-$	0.198	45
$=\text{C}-$	0.198	36
$=\text{C}=\text{}$	0.198	36
$\equiv\text{CH}$	0.153	(36) ^c
$\equiv\text{C}-$	0.153	(36)
Ring increments		
$-\text{CH}_2-$	0.184	44.5
$-\text{CH}-$	0.192	46
C (in ring)	(0.154)	(31)
$=\text{CH}-$	0.154	37
$=\text{C}-$	0.154	36
$=\text{C}=\text{}$	0.154	36

(continued)

TABLE 12-12 (Continued)

Increment	ΔP	ΔV
Halogen increments		
-F	0.224	18
-Cl	0.320	49
-Br	(0.50)	(70)
-I	(0.83)	95
Oxygen increments		
-OH (alcohols)	0.06	(18)
-OH (phenols)	-0.02	(3)
-O- (nonring)	0.16	20
-O- (ring)	(0.12)	(8)
$\begin{array}{c} \\ -C=O \end{array}$ (nonring)	0.29	60
$\begin{array}{c} \\ -C=O \end{array}$ (ring)	(0.20)	(50)
$\begin{array}{c} \\ HC=O \end{array}$ (aldehyde)	0.33	73
-COOH (acid)	0.40	80
-COO- (ester)	0.47	80
=O (exc. for above combinations)	0.12	11
Nitrogen increments		
-NH ₂	0.095	28
$\begin{array}{c} \\ -NH \end{array}$ (nonring)	0.135	(37)
$\begin{array}{c} \\ -NH \end{array}$ (ring)	(0.09)	(27)
-N- (nonring)	0.17	(42)
$\begin{array}{c} \\ -N- \end{array}$ (ring)	(0.13)	(32)
-CN	(0.36)	(80)
-NO ₂	(0.42)	(78)

(continued)

TABLE 12-12 (Continued)

Increment	ΔP	ΔV
Sulfur increments		
-SH	0.27	55
-S- (nonring)	0.27	55
-S- (ring)	(0.24)	(45)
=S	(0.24)	(47)

- a. There are no increments for hydrogen.
 b. All bonds shown as free are connected to atoms other than H.
 c. Values in parentheses are based upon too few experimental values to be reliable [24].

Source: Reid and Sherwood [24].

(3) From Eq. 12-5

$$\begin{aligned}\theta &= 0.567 + (0.072) - (0.072)^2 \\ &= 0.634\end{aligned}$$

(4) From Eq. 12-18

$$\begin{aligned}P_c &= \frac{58.13}{(0.340 + 0.891)^2} \\ &= 38.4 \text{ atm}\end{aligned}$$

(5) From Eq. 12-19

$$\begin{aligned}V_c &= 40 + 216 \\ &= 256 \text{ cm}^3/\text{mol}\end{aligned}$$

(6) From Eq. 12-17

$$\begin{aligned}\beta &= \frac{[(1 - 0.634)^{2/7} - 0.048] \ln(256) + [1 - 0.634]^{2/7} \ln(38.4) + 1.255}{[1 - 0.634]^{2/7}} \\ &= 10.51\end{aligned}$$

(7) From Eqs. 12-16 and 12-4

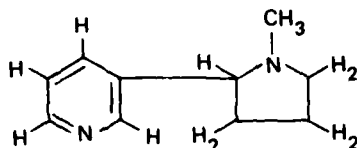
$$\begin{aligned}T_b &= \frac{(0.634) e^{10.51}}{82.05} \\ &= 283.4 \text{ K}\end{aligned}$$

$$\text{Error} = 20.4\text{K}$$

The measured boiling point of isobutane is 263.0K; thus, this method shows a relative error of 7.8%.

Example 12-7 Estimate T_b for nicotine (molecular weight = 162.24).

(1) Sketch nicotine



(2) From Tables 12-6 and 12-12

	$\frac{\Delta T}{\Delta P}$	$\frac{\Delta P}{\Delta V}$	$\frac{\Delta V}{\Delta T}$
1(-CH ₃)	0.020	0.227	55
3(-CH ₂ ring)	3(0.013)	3(0.184)	3(44.5)
1(-CH ring)	0.012	0.192	46
2(-N ring)	2(0.007)	2(0.13)	2(32)
4(=CH ring)	4(0.011)	4(0.154)	4(37)
1(=C- ring)	0.011	0.154	36
	$\Sigma \Delta T = 0.140$	$\Sigma \Delta P = 1.871$	$\Sigma \Delta V = 482.5$

(3) From Eq. 12-5

$$\begin{aligned}\theta &= 0.567 + (0.140) - (0.140)^2 \\ &= 0.687\end{aligned}$$

(4) From Eq. 12-18

$$\begin{aligned}P_c &= \frac{162.24}{(0.34 + 1.871)^2} \\ &= 33.2 \text{ atm}\end{aligned}$$

(5) From Eq. 12-19

$$\begin{aligned}V_c &= 40 + 482.5 \\ &= 522.5\end{aligned}$$

(6) From Eq. 12-17

$$\beta = \frac{[(1 - 0.687)^{2/7} - 0.048] \ln(522.5) + [1 - 0.687]^{2/7} \ln(33.2) + 1.255}{[1 - 0.687]^{2/7}}$$
$$= 11.09$$

(7) From Eqs. 12-16 and 12-14

$$T_b = \frac{(0.687) e^{11.09}}{82.05}$$
$$= 549\text{K}$$

Error = +30K

The measured boiling point of nicotine is 519.2K; thus, this method shows a relative error of 5.8%.

12-6 METHOD OF OGATA AND TSUCHIDA

Principles of Use. Ogata and Tsuchida [20] found a linear relationship for estimating normal boiling points for compounds of the form RX, where R is a hydrocarbon radical and X is a hydrogen atom or a functional group. The equation takes the form:

$$T_b = py + q \quad (12-20)$$

where T_b is the normal boiling point (K), y is a function of the hydrocarbon group(s) contained in the compound, and p and q are constants characteristic of the functional group attached to the hydrocarbon group. For a group of 600 compounds tested by Ogata and Tsuchida, boiling points for 80% deviate by less than 2°C from known values and 98% deviate by less than 5°C .

The method is not without limitations, however: it cannot treat compounds containing more than one functional group, and the range of hydrocarbon fragments for which y values are known is small. For example, it is unsuitable for compounds with condensed or fused rings, such as naphthalene or anthracene, and for dihalogenated compounds. Tables 12-13 and -14 list the values of y , p , and q determined by Ogata and Tsuchida.

TABLE 12-13

Values of y for Equation 12-20

R	y	R	y
Methyl	55.5	t-Amyl	122.0
Ethyl	77.1	Neopentyl	125.0
n-Propyl	102.0	n-Hexyl	171.0
Isopropyl	92.0	Isohexyl	168.0
n-Butyl	124.5	n-Heptyl	191.5
sec-Butyl	118.0	n-Octyl	210.0
Isobutyl	116.5	Vinyl	71.0
t-Butyl	96.0	Allyl	104.0
n-Amyl	149.0	2-Butenyl	127.0
Isoamyl	140.5	Phenyl	197.0

Source: Ogata and Tsuchida [20]

Basic Steps

- (1) Determine that the compound consists of one or more hydrocarbon radicals and no more than one functional group.
- (2) Determine the value of y from Table 12-13, using the largest hydrocarbon radical for R. (If this is not possible, use a different method.)
- (3) Determine values of p and q from Table 12-14.
- (4) Compute T_b by substituting y , p , and q values in Eq. 12-20.

Example 12-8 Estimate the boiling point of diphenyl sulfide.

- (1) For the phenyl group, from Table 12-13,

$$y = 197.0$$

- (2) For R-S-R, from Table 12-14,

$$p = 1.937, q = 214.4$$

- (3) Using Eq. 12-20,

$$T_b = 1.937 (197.0) + 214.4 = 596.0\text{K}$$

TABLE 12-14

Values of Parameters p and q for Equation 12-20

RX	p	q	R Groups with Deviations >5K	RX	p	q	R Groups with Deviations >5K
PH	1.615	63.8	Me, t-Bu	HCOR	1.140	233.8	
RCI	1.348	179.7		MeCOR	1.022	270.6	
RBr	1.260	213.6		EtCOR	0.918	302.2	
RI	1.198	253.4		RCN	0.960	292.2	
ROH	0.096	277.6	Me, t-Bu	RCOCl	1.040	267.9	
MeOR	1.217	191.2	Me	HCOOR	1.073	244.6	
EtOR	1.137	221.8	Me, Hep	MeCOOR	1.000	273.2	
ROR	2.158	143.2		EtCOOR	0.963	297.5	
PhOR	0.849	377.4		PhCOOR	0.766	425.9	
RONO ₂	1.016	280.5		RCOOH	0.903	342.4	
RSH	1.191	221.0	Me	RCOOMe	1.000	273.2	
RSMc	1.146	249.2		RCOOEt	0.963	297.5	
RSEt	1.080	280.0		RCOOPr	0.911	323.4	
RSR	1.937	214.4	Me, Hep	RCOOPh	0.766	425.9	
RNH ₂	1.194	201.4	Me	(RCO) ₂ O	1.286	337.7	Hep
RNHMe	1.180	215.2		ClCH ₂ COOR	0.721	359.6	
RNHEt	1.081	247.9		Cl ₂ CHCOOR	0.745	372.3	
RNHPPr	0.991	282.8		BrCH ₂ COOR	0.745	374.4	
RNMe ₂	1.193	218.7	Me, Et	NCCH ₂ COOR	0.565	433.5	
RNO ₂	0.923	308.8		CH ₂ =CHCOOR	0.918	302.2	

Source: Ogata and Tsuchida [20]

Error = 26.8K

The measured boiling point of diphenyl sulfide is 569.2K; thus, this method shows a relative error of 4.7%.

Example 12-9 Estimate the boiling point of ethylene.

(1) For CH₂=CH-, Table 12-13 lists

$$y = 71.0$$

(2) For RH, Table 12-14 lists

$$p = 1.615, q = 63.8$$

$$(3) T_b = 1.615 (71.0) + 63.8 = 178.5K$$

$$\text{Error} = 9.1K$$

The measured boiling point of ethylene is 169.4K; thus, this method shows a relative error of 5.4%.

12-7 METHOD OF SOMAYAJULU AND PALIT

Principles of Use. Somayajulu and Palit [25] developed a method for estimating the boiling points of normal hydrocarbons that contain no more than one functional group. Their method is a three-parameter fitting of data for homologous series of compounds with respect to the sum of the atomic numbers for individual atoms in the compound. Equation 12-21 describes the correlation:

$$T_b = r (\Sigma Z)^t + s \quad (12-21)$$

where T_b is the normal boiling point (K), ΣZ is the sum of the atomic numbers for the individual atoms in the compound, and r , s , and t are parameters dependent upon the homologous series. Table 12-15 lists atomic numbers for some elements commonly found in organic compounds, and Table 12-16 lists values for r , s , and t . Boiling points estimated by this method are about as accurate as those calculated by the method of Ogata and Tsuchida.

Basic Steps

- (1) Obtain ΣZ by summing the atomic numbers of all the atoms in the compound.
- (2) Obtain values for r , s , and t from Table 12-16.
- (3) Compute T_b from Eq. 12-21.

Example 12-10 Estimate the normal boiling point of acetaldehyde and acetic acid.

- For acetaldehyde (CH_3CHO):

$$(1) \Sigma Z = 2 (6) + 4 (1) + 8 = 24$$

$$(2) \text{ From Table 12-16, } r = 48.87, s = 36.85, t = 1/2$$

TABLE 12-15

Atomic Numbers of Some Common Elements

Element	At. No.	Element	At. No.
Br	35	I	53
C	6	N	7
Cl	17	O	8
F	9	P	15
H	1	S	16

TABLE 12-16

Values of r, s, and t for Equation 12-21

Homologous Series	r	s	t
n-Alkyl fluorides	51.31	-26.70	$\frac{1}{2}$
n-Alkyl chlorides	52.06	-17.05	$\frac{1}{2}$
n-Alkyl bromides	57.54	-102.5	$\frac{1}{2}$
n-Alkyl iodides	61.10	-164.0	$\frac{1}{2}$
n-Alkyl aldehydes	48.87	36.85	$\frac{1}{2}$
n-Alkyl ketones	44.11	67.20	$\frac{1}{2}$
n-Alkyl acids	36.17	188.0	$\frac{1}{2}$
n-Alkyl primary amines	45.43	55.56	$\frac{1}{2}$
n-Alkyl secondary amines	46.52	28.10	$\frac{1}{2}$
n-Alkyl tertiary amines	47.95	-5.05	$\frac{1}{2}$
n-Alkyl benzenes	46.88	52.57	$\frac{1}{2}$
n-Alkyl cyclohexanes	49.54	9.16	$\frac{1}{2}$
n-Alkyl cyclohex-1-enes	47.24	34.10	$\frac{1}{2}$
n-Alkanes	154.40	-223.90	$\frac{1}{3}$
n-Alk-1-enes	154.45	-222.10	$\frac{1}{3}$
n-Alk-1-yne	144.44	-168.78	$\frac{1}{3}$
Normal alcohols	2.44	288.0	1
n-Alkyl ethers	3.58	157.10	1
n-Alkyl acetates	2.76	220.80	1
n-Alkanethiols	3.87	178.0	1

Source: Somayajulu and Palit [25]

$$(3) \text{ From Eq. 12-21, } T_b = 48.87 (24)^{1/2} + 36.85 = 276.3\text{K}$$

$$\text{Error} = -17.7\text{K}$$

The measured boiling point of acetaldehyde is 294.0K; thus, this method shows a relative error of -6.0%.

- For acetic acid (CH_3COOH):

$$(1) \quad \Sigma Z = 2 (6) + 4 (1) + 2 (8) = 12$$

$$(2) \quad \text{From Table 12-16, } r = 36.17, s = 188.0, t = 1/2$$

$$(3) \quad \text{From Eq. 12-21, } T_b = 36.17 (32)^{1/2} + 188.0 = 392.6\text{K}$$

$$\text{Error} = 1.6\text{K}$$

The measured boiling point of acetic acid is 391.0K; thus, this method shows a relative error of 0.4%.

12-8 KINNEY'S METHOD

Principles of Use. Kinney's method [11, 12] can be used to estimate the boiling points of aliphatic hydrocarbons, olefins, and naphthenes. The results deviate from measured values by less than 10K for many compounds tested. In this method, the boiling point is considered to be a function of the "boiling-point number," Y:

$$T_b = 230.1 Y^{1/3} - 270 \quad (12-22)$$

where T_b is the boiling point (K). The value of Y is determined by adding contributions from the structural groups of the molecule as listed in Table 12-17.

Some care must be exercised in the sequence of contributions added, since the individual contributions to Y are not commutative. The longest chain in the molecule is designated as the main chain or base group for the molecule. The contributions from atoms in the base group are totaled first. Contributions from branching groups are then totaled, followed by olefinic groups and rings. (Rings are always considered to be side groups attached to the base group; for cycloalkanes, such as cyclohexane, the ring is a side group attached to the base group, which is a hydrogen.) An additional consideration is that if two equal chain lengths are possible choices for the base group, the one containing the fewer unsaturated linkages is used.

TABLE 12-17

Atomic and Group Boiling Point Numbers

Structural Group	ΔY	Structural Group	ΔY
Carbon in main chain	0.8	Diolefins:	
Hydrogen attached to main chain	1.0	Allenenes	4.8
Radicals, saturated, attached to main chain or to cyclic rings:		Conjugated	a + 0.8
Methyl	3.05	Not conjugated	a
Ethyl	5.5	Triolefins:	
Propyl	7.0	All bonds conjugated	a + 2.4
Butyl	9.7	Two bonds conjugated	a + 0.8
2,2-Dimethyl grouping (in addition to value for each methyl)	-0.4	No conjugation	a
Multiple alkyls attached to adjacent carbons of saturated main chains of six carbons or less:		Diacetylenes:	
2-3 alkyls	0.5	1,3-Diacetylenes	b
4 or more alkyls	1.0	All other conjugated	b + 3.0
Olefinic linkages:		No conjugation	b
$\text{CH}_2=\text{CH}_2$	1.2	Enynes:	
$\text{RCH}=\text{CH}_2$	1.5	Conjugated	c + 0.8
$\text{RCH}=\text{CHR}$	1.9	No conjugation	c
$\text{R}_2\text{C}=\text{CHR}$	2.3	Dienynes:	
$\text{R}_2\text{C}=\text{CR}_2$	2.8	Conjugated	c + 2.4
Radicals, unsaturated, attached to main chain:		No conjugation	c
Methylene	4.4	Cyclic radicals:	
Ethylidene	7.0	Each carbon	0.8
Vinyl	5.4	Each hydrogen	1.0
Propylidene	9.0	Unsaturated linkages	c
Butylidene	10.4	Ring:	
Acetylenic linkages:		Cyclopropyl	2.1
$\text{HC}\equiv\text{CH}$	4.0	Cyclobutyl	2.3
$\text{RC}\equiv\text{CH}$	4.4	Cyclopentyl	2.5
$\text{RC}\equiv\text{CCH}_3$	5.4	Cyclohexyl	2.7
$\text{RC}\equiv\text{CR}$	4.8	Cycloheptyl	3.4
		Cyclooctyl	3.9
		Cyclononyl	4.4
		Cyclodecyl	4.9
		Cyclohendecyl	5.4
		Cyclododecyl	5.9
		Cyclotridecyl	6.4
		Cyclotetradecyl	6.9
		Cyclopentadecyl	7.4
		Cyclohexadecyl	7.9
		Cycloheptadecyl	8.4

a. Normal value of double bonds.

b. Normal value of triple bonds.

c. Normal value of bonds.

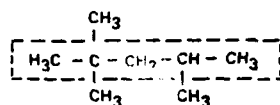
Source: Kinney [11,12]

Basic Steps

- (1) Draw the compound structure.
- (2) Determine the base group or main chain; this is the longest chain in the compound or, if two equal length chains are possible, the one with the fewer unsaturated linkages.
- (3) Add the contributions to Y from the main chain, using Table 12-17.
- (4) Add the contributions to Y for any branching groups.
- (5) Add the contributions to Y for any unsaturated linkages and/or rings.
- (6) Compute T_b from Eq. 12-22.

Example 12-11 Estimate the boiling point of isooctane.

- (1) Draw the structure



- (2) Determine the main chain (dashed box).
- (3) From Table 12-17, the contributions from the main chain are

$$\begin{aligned} Y_{\text{main}} &= 5C + 9H \\ &= 5(0.8) + 9(1.0) = 13.0 \end{aligned}$$

- (4) Contributions from the side chains are

$$Y(2,2\text{-dimethyl}) = 2(3.05) - 0.4 = 5.7$$

$$Y(4\text{-methyl}) = 3.05$$

$$\text{Total } Y_{\text{branch}} = 3.05 + 5.7 = 8.75$$

- (5) $Y_{\text{total}} = Y_{\text{main}} + Y_{\text{branch}}$

$$= 13.0 + 8.75 = 21.8$$

- (6) From Eq. 12-22,

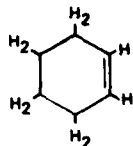
$$T_b = 230.1(21.8)^{1/3} - 270 = 373\text{K}$$

$$\text{Error} = 1\text{K}$$

The measured boiling point of isooctane is 372.4K; thus, this method shows a relative error of 0.3%.

Example 12-12 Estimate the boiling point of cyclohexene.

- (1) Draw the structure



- (2) The base group is H.

(3) $Y_{\text{base}} = 1.0$

(4) $Y_{\text{ring}} = 6 (\text{C}) + 9 (\text{H}) + \text{cyclohexyl group}$
 $= 6 (0.8) + 9 (1.0) + 2.7 = 16.5$

$$Y_{\text{double bond}} = 1.9$$

(5) $Y_{\text{total}} = Y_{\text{base}} + Y_{\text{ring}} + Y_{\text{double bond}}$
 $= 1.0 + 16.5 + 1.9 = 19.4$

(6) $T_b = 230.1 (19.4)^{1/3} - 270 = 348 \text{ K}$

$$\text{Error} = -8 \text{ K}$$

The measured boiling point of cyclohexene is 356.1K; thus, this method shows a relative error of -2.2%.

12-9 METHOD OF STIEL AND THODOS

Principles of Use. The method of Stiel and Thodos [26] is applicable only to saturated aliphatic hydrocarbons. Their method involves the use of two equations. One of these (Eq. 12-23) is used to estimate the boiling point of normal hydrocarbons:

$$T_{b_n} = 1209 - \frac{1163}{1 + 0.0742 (N^{0.85})} \quad (12-23)$$

where T_{b_n} is the boiling point (K) and N is the number of carbons in the compound. The second equation is used to determine the boiling point of isomeric (branched) saturated hydrocarbons:

$$T_{b_{\text{isomer}}} = T_{b_n} - \left[\left(\frac{96.52}{N^2} \right) (W_n - W_i) + 5.45 (P_n - P_i) \right] \quad (12-24)$$

The terms W_n and W_i are the Wiener numbers of the normal hydrocarbon and the isomer respectively, and P_n and P_i are the polarity numbers for the normal hydrocarbon and the isomer respectively.

The Wiener number of a normal hydrocarbon can be computed from the total number of carbons in the molecule by Eq. 12-11 (repeated here for convenience):

$$W_n = \frac{(N-1)(N)(N+1)}{6} \quad (12-11)$$

For an isomer, the Wiener number is computed by multiplying together the number of carbon atoms on each side of a carbon-to-carbon bond, repeating this for all of the carbon-to-carbon bonds in the molecule, and then summing the products.

The polarity number is defined as the number of pairs of carbon atoms in the molecule that are separated by exactly three bonds. For normal hydrocarbons, the calculation of P_n is exceedingly simple:

$$P_n = N-3 \quad (12-25)$$

The basic steps and examples below further explain the calculation of W_i and P_i .

Basic Steps

- (1) Determine the number of carbons in the compound, N .
- (2) Compute T_{b_n} from Eq. 12-23.
- (3) If the molecule is a straight chain, T_{b_n} is the boiling point of the compound.
- (4) If the molecule is branched, draw the structure.
- (5) Compute W_n and P_n from Eqs. 12-11 and 12-25.
- (6) Compute P_i by counting the number of pairs of carbons that are separated by three bonds.
- (7) Compute W_i by counting carbons on both sides of a single bond (C-C bonds only). Multiply the numbers together and sum the products for all of the single bonds in the molecule.
- (8) Compute $T_{b_{\text{isomer}}}$ from Eq. 12-24, using the value of T_b estimated in step 2.

Example 12-13 Estimate the boiling point of n-hexane.

(1) $N = 6$

(2) From Eq. 12-23,

$$T_{b_n} = 1000 \left[1.209 - \frac{1.163}{1 + 0.0742 (6)^{0.85}} \right] = 341\text{K}$$

Error = -1K

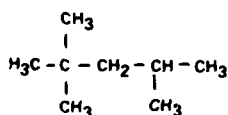
The measured boiling point of n-hexane is 342K; thus, this method shows a relative error of -0.3%.

Example 12-14 Estimate the boiling point of isooctane.

(1) $N = 8$

(2) $T_{b_n} = 1000 \left(1.209 - \frac{1.163}{1 + 0.0742 (8)^{0.85}} \right) = 398\text{K}$

(3) The structure is



(4) $W_n = \frac{7 \times 8 \times 9}{6} = 84$

$P_n = 8 - 3 = 5$

(5) $P_i = 5$

(6) $W_i = (1 \times 7) + (1 \times 7) + (1 \times 7) + (4 \times 4) + (5 \times 3) + (1 \times 7) + (1 \times 7) = 66$

(7) $T_{b_{\text{isomer}}} = 398 - \left[\frac{(96.52)}{8^2} (84 - 66) + 5.45 (5 - 5) \right] = 371\text{K}$

Error = -1K

The measured boiling point of isooctane is 372.4K; thus, this method shows a relative error of -0.4%.

12-10 FACTORS AFFECTING BOILING POINT [1,17]

Each of the preceding seven methods yields a value for the normal boiling point of a pure compound. If the pressure on the liquid differs from one atmosphere, or if the liquid contains impurities, the boiling point observed for the compound differs from that estimated for the pure compound in a predictable fashion. This section briefly discusses the ways in which an estimated normal boiling point can be adjusted to compensate for impurities and/or pressures other than one atmosphere.

Impurities in a compound alter its observed boiling point by changing the vapor pressure of the liquid. If the impurity is non-volatile, such as sugar in water, and the solution is dilute, the vapor pressure of the liquid obeys Raoult's law:

$$P = X_A P_{vp} \quad (12-26)$$

where X_A is the mole fraction of the solvent (i.e., compound of interest), P is the vapor pressure of the solution, and P_{vp} is the vapor pressure of the pure liquid at $X_A = 1$. If X_B is the mole fraction of the solute, Eq. 12-26 may be rewritten as:

$$P = (1 - X_B) P_{vp} \quad (12-27)$$

or

$$\frac{P_{vp} - P}{P_{vp}} = X_B \quad (12-28)$$

The solution cannot boil until its temperature is sufficiently above the boiling point of the pure solvent to compensate for the pressure decrease noted above. An equation that expresses this concept is obtained by combining the Clausius-Clapeyron equation (see Chapters 13 and 14) with Eq. 12-28 in such a way as to balance the vapor pressure decrease due to the presence of the impurity with an increase in the vapor pressure due to temperature:

$$\Delta T_b = \frac{RT_b^2}{\Delta H_v} \quad \Delta X_B = \frac{RT_b^2}{\Delta H_v} X_B \quad (12-29)$$

where T_b is the normal boiling point temperature, ΔT_b is the change in temperature from the normal boiling point due to the solute, R is the universal gas constant (1.9872 cal/mol-K), and ΔH_v is the enthalpy of

vaporization (cal/mol). $\Delta X_B = X_B$, since $X_B = 0$ in a pure compound. To estimate the boiling point of a compound containing impurities, first estimate the normal boiling point as outlined previously; then estimate ΔH_{vap} by the methods presented in Chapter 13. Substitute these values and the mole fraction of solute (X_B) in Eq. 12-29 to compute the boiling point elevation. Finally, add ΔT_b to T_b to obtain the boiling point of the impure material.

For compounds that dissociate, such as sodium chloride in water, the situation is somewhat more complicated. The mole fraction term used throughout this discussion is a measure of the number of particles of non-solvent species in the solution, which depends on the extent of dissociation. If the solute dissociates completely into two ions for each molecule, the number of particles contributing to the boiling point elevation would be twice as many as would exist if there were no dissociation. The degree of dissociation depends on the concentration of the impurity and its dissociation constant. In estimating the boiling points of impure compounds, the impurity is assumed to dissociate completely, and its mole fraction in Eq. 12-29 is expressed accordingly. That is, if the impurity compound dissociates into two ions, its mole fraction (X_B) is

$$X_B = \frac{2M_B}{2M_B + M_A} \quad (12-30)$$

where M_B = moles of impurity present before dissociation and M_A = moles of compound whose boiling point is being estimated. M_B is multiplied by 2 because each molecule forms two ions when it dissociates. The assumption of complete dissociation causes little error compared with those entailed in estimating the normal boiling point and the enthalpy of vaporization.

Boiling points at pressures other than one atmosphere can be estimated by using the Clausius-Clapeyron equation in the following form:

$$\ln P - \ln P_b = \frac{\Delta H_v}{R} \left(\frac{1}{T_b} - \frac{1}{T} \right) \quad (12-31)$$

where P is the pressure on the actual sample (mm Hg) and P_b is the pressure at the normal boiling point (760 mm Hg). Using known values of P and P_b and estimated values of ΔH_v and T_b in Eq. 12-31, one can calculate the observed boiling point for a compound under pressures other than one atmosphere.

12-11 AVAILABLE DATA

Boiling points are listed in many texts. Users should be careful to note the pressures at which the temperatures were measured. Some general references are listed in Appendix A. The following contain complementary information and are recommended:

Dean, J.A. [5] General data including boiling points for many organic and inorganic compounds.

Reid, R.C., *et al.* [23] Appendix with tabulation of normal boiling points and critical constants for many organic compounds.

Stull, D.R. and Prophet, H. [27] Tabulation of thermochemical properties of inorganic compounds.

Vargaftik, N.B. [31] General data on thermochemical properties of liquids and gases.

Weast, R.C. [33] General data including boiling points for many organic and inorganic compounds.

Windholtz, M. [34] General data including boiling points for chemicals and drugs.

12-12 SYMBOLS USED

- a = van der Waal's constant in Eq. 12-6
- B = chemical class constant in Eq. 12-1
- b = van der Waal's constant in Eq. 12-6
- f_a, f_b = correction factors for branched hydrocarbons in Forman-Thodos method, Eqs. 12-7 to 12-10
- ΔH_v = enthalpy of vaporization in §12-10 (cal/mol)
- K_1, K_2, K_3, K_4 = functional group constants in Eqs. 12-12, -13
- m = number of side chains in Eqs. 12-9, -10
- M = molecular weight in Eqs. 12-2, 12-3 and 12-18 (g/mol)
- M_A = moles of solvent or "pure" compound in Eq. 12-30
- M_B = moles of impurity in Eq. 12-30
- N = number of carbon atoms in saturated aliphatic hydrocarbon in Eqs. 12-23, -24
- n = sum of carbon and functional atoms for Forman-Thodos method of estimating critical temperature

n_D	= refractive index measured relative to the sodium D line in Eq. 12-2
P	= vapor pressure of solution in §12-10 (mm Hg); also (with appropriate subscript) polarity number in Eqs. 12-24, -25
P_c	= critical pressure of a compound (atm) in Eqs. 12-15, -17 and -18
P_{vp}	= vapor pressure of pure compound in §12-10 (mm Hg)
$[P]$	= parachor in Eqs. 12-1, -3
ΔP	= Lydersen pressure increment in Table 12-12 and Eq. 12-18
p	= functional group constant in Eq. 12-20
q	= functional group constant in Eq. 12-20
R	= universal gas constant = 82.05 atm-cm ³ /mol-K in Eq. 12-6 = 1.9872 cal/mol-K in Eq. 12-29
$[R_D]$	= molar refraction measured relative to sodium D line in Eqs. 12-1, -2
r	= parameter in Eq. 12-21
s	= parameter in Eq. 12-21
T_b	= normal boiling point (K)
T_c	= critical temperature (K)
ΔT	= Lydersen increment for computing θ in Eq. 12-5
t	= parameter in Eq. 12-21
V_b	= saturated liquid molal volume at the boiling point in Eq. 12-14 (cm ³ /g-mole)
V_c	= critical volume of a compound (cm ³ /mol) in Eqs. 12-14, -17 and -19
ΔV	= Lydersen volume increment in Table 12-12 and Eq. 12-19
W	= Wiener number
X_A	= mole fraction of solvent in solution
X_B	= mole fraction of impurity in solution
Y	= boiling point number in Eq. 12-22
y	= parameter in Eq. 12-20
Z	= atomic number in Eq. 12-21
Z_c	= critical compressibility factor in Eq. 12-15

Greek:

- β = parameter in Eqs. 12-16 and 12-17
 σ = surface tension in Eq. 12-3 (dynes/cm)
 θ = ratio T_b/T_c in Eqs. 12-4, 12-5, 12-15 and 12-17
 ρ_L = liquid density in Eqs. 12-2, -3 (g/mL)
 ρ_v = vapor density in Eq. 12-3 (g/mL)

Subscripts:

- i = isomeric alkane
n = normal alkane

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13

HEAT OF VAPORIZATION

Carl E. Rechsteiner, Jr.

13-1 INTRODUCTION

The heat of vaporization, ΔH_v (also called the latent heat of vaporization, heat of evaporation, or enthalpy of vaporization) is defined as the quantity of heat required to convert a unit mass of liquid into a vapor without a rise in temperature, which implies a constant-pressure process [1]. It is a function of temperature and decreases with increasing temperature; values have been tabulated for many compounds [6,23,34]. The ability to estimate the heat of vaporization is helpful for checking values reported in the literature, but its most important use is in estimating other physico-chemical properties. The parameter is also required in some chemical spill models.

Since the early 1900s, the preferred method for measuring ΔH_v has been to determine the quantity of electrical energy needed to vaporize a unit mass of liquid at a constant temperature. Values obtained with this method are highly reproducible and may be very accurate if all heat losses from the experimental apparatus are accounted for. Prior to 1900, heats of vaporization were determined by measuring the heat of condensation of the vapor; this routinely gave lower values, sometimes exceeding 10%, than those obtained with the present method. Unfortunately, some values obtained by the heat of condensation method are still included in some reference tabulations [8].

The heat of vaporization is a basic thermodynamic quantity and, as such, has theoretical importance. The entropy of vaporization at any temperature may be determined from the ratio of the heat of vaporization at that temperature to the temperature. The vapor pressure of a material at some temperature is frequently estimated by use of the Clapeyron equation or one of its rearrangements, all of which use ΔH_v as an input parameter.

13-2 AVAILABLE ESTIMATION METHODS

Many equations have been proposed for estimating heats of vaporization of organic compounds. Although the methods proposed range from those based on theory to those based on empirical factors, most incorporate a mixture of the two approaches. The most frequent starting point for the proposed relations is some form of the Clapeyron equation, which is modified as necessary and then fit to a set of experimental data to determine the best-fit parameters.

One of the earliest estimation methods for the heat of vaporization of organic compounds was developed by F. Trouton (ca. 1884), who noted that the ratio between the heat of vaporization and the normal boiling point is essentially a constant: 21 cal/deg-mol.

Three authors — Bakker, Batschinsky, and Partington — have proposed relationships for calculating heats of vaporization from critical data using strictly theoretical considerations [20]. Although these methods have shown some success for limited groups of compounds, Fish-tine [7] examined the proposed methods with a number of common chemicals and frequently encountered errors of 30%-40%.

Many authors have proposed semiempirical equations for predicting heats of vaporization from critical constants. Haggemacher [11], Viswanath and Kuloor [28], Meissner [15], Watson [31], Klein [14a], and Giacalone (in Ref. 21) developed correlations based on the Clapeyron equation modified by the compressibility-factor equation of state. The differences among them reflect varying assumptions with respect to the difference between the vapor and liquid compressibilities and the relationship between the temperature and the vapor pressure of the compound. Riedel [25], Lydersen (in Ref. 24), Chen [4], and Pitzer [22] have proposed methods based on Van der Waal's theory of corresponding states; all include a correlating parameter to improve estimation accuracy.

Another group of methods is based on the Thiessen relation, which describes ΔH_v as a function of the reduced temperature (the ratio between the measured temperature and the critical temperature). A number of researchers, such as Watson [32], Nutting [18], Winter [33], and Bowden [2], utilize the ratio of this relation at two temperatures to estimate ΔH_v at one temperature from its value at the other temperature. These methods differ in the value of the exponent in the Thiessen equation. Silverberg and Wenzel [27a] computed the Thiessen exponent for a number of compounds for a range of temperatures below the critical temperature. Although the value ranged from 0.237 to 0.389, the average (0.379) differs by less than 1% from the 0.38 proposed by Watson [32].

Other workers have included Thiessen's equation in developing the "lyoparachor," a temperature-independent additive property of structure analogous to the parachor. Winter [33], Bowden and Jones [3], and Chu [5] have been involved in this effort. Sastri *et al.* [26] have incorporated many of these previous researchers' ideas into a generalized procedure that requires only the compound structure as input for estimating the heat of vaporization at the normal boiling point.

Other attempts have been made to correlate the heat of vaporization with compound structure or structure-related features. Kistiakowsky (in Ref. 10) developed a correlation between ΔH_v and the normal boiling point for nonpolar compounds. Fishtine [10] extended the range of applicability of this equation to other compounds by introducing a constant based on a function of dipole moment. The Kistiakowsky method is described in detail in §14-3 as part of Method 1 for the estimation of vapor pressure. The specific relationship for estimating $\Delta H_{v,b}$ by the Kistiakowsky method is found in Eq. 14-16 with supporting data in Table 14-4. The accuracy of this method is comparable to those listed in Table 13-2.

Narsimhan [16,17] developed correlations for alcohols, phenols, and fatty acid esters based on their molecular weight, vapor and liquid densities, and molar volume at the critical point. Graph-theory approaches, such as that of Kier and Hall [13] or Ogden and Liemezs [19], have also been proposed.

The methods recommended in this chapter were chosen for their general accuracy (typically 2% error or less) and ease of calculation. Their input parameters are frequently available in the literature or may be readily estimated.

13-3 SELECTION OF APPROPRIATE METHOD

The methods recommended for estimating heats of vaporization are listed in Table 13-1 along with their theoretical bases, required input parameters, and application ranges. Table 13-2 compares the accuracies of the methods, using various literature references and known values of the required input parameters, such as T_b , T_c , and P_c . All of these methods show average deviations from literature values of less than 5%. If input parameters must be estimated, the uncertainty of ΔH_v may, of course, be higher. Typical errors in estimating T_b and T_c by the methods of Chapter 12 are about 2% to 4%; estimates of P_c usually deviate by about 4% to 8% from measured values.¹

All methods recommended for predicting heats of vaporization require similar input data. When the boiling point, T_b , the critical temperature, T_c , and the critical pressure, P_c , are known or readily estimated, use the methods described in §13-4. If either P_c or T_c is not available, use the Haggmacher method (§13-5); in addition, if no vapor pressure data are available, use the Sastri method (§13-6). To estimate heats of vaporization at temperatures other than the boiling point, use the Watson method (§13-7), calculating the heat of vaporization at the boiling point, ΔH_{vb} , by one of the other recommended methods. More reliable estimates will be obtained if ΔH_{vb} is calculated by several of the recommended methods, but this is not always possible.

13-4 ESTIMATION OF ΔH_{vb} FROM CRITICAL CONSTANTS

Principles of Use. A number of methods based on critical temperature and pressure have been proposed for estimating ΔH_{vb} , the heat of vaporization at the normal boiling point. Four of them appear to have the widest applicability and generally estimate ΔH_{vb} within 2% with maximum errors of about 6%. Two of the methods, the modified Klein and the Giacalone, are based on the Clapeyron equation; the other two methods, those of Riedel and Chen, were derived empirically.

The Clapeyron equation (13-1) is the basic expression for describing the shape of the vapor pressure curve for any material as a function of the temperature and certain properties of the material:

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_g - V_l)} \quad (13-1)$$

1. The propagation of errors in the estimation of physico-chemical properties is discussed in Appendix C.

TABLE 13-1
Summary of Recommended Methods for Estimating Heats of Vaporization

Section	Method	Basis	Input Parameters ^a	Application Range	Comments
13-4	Modified Klein [8]	Clapeyron equation	T_b, T_c, P_c	All compounds at T_b	Constant in equation is a function of T_b
	Giacomoni [8,21]	Clapeyron equation	T_b, T_c, P_c	Nonhydrocarbon, polar organics at T_b	
	Riedel [25]	Clapeyron equation	T_b, T_c, P_c	Nonpolar and slightly polar organics at T_b	
	Chen [4]	Clapeyron equation, empirical fit	T_b, T_c, P_c	Entire liquid range if vapor pressure at T of interest is known	Primarily used at T_b
13-5	Haggenmacher [9,11]	Clapeyron equation	T_b, T_c, P_c	$T \leq T_b$	Antoine's constants B and C may be estimated. ΔH_v can be computed if T_c and P_c unknown.
		plus Antoine's equation	Antoine's constants B and C		
13-6	Sastri [26]	Lyoparachor	Compound structure	at T_b	
13-7	Watson [31]	Thiessen's equation	T_c and ΔH_v at some temperature	Entire liquid range	

a. T_b, T_c may be estimated by methods of Chapter 12 if unknown. P_c may be estimated, if unknown, by methods provided in §13-4 of this chapter.

TABLE 13-2
Accuracy of Estimation Methods for Heat of Vaporization
 (Average percent error)

Literature Reference ^a	Method ^b					
	Modified Klein [14a]	Giacalone [9,17]	Riedel [25]	Chen [4]	Haggenmacher [11,12]	Sastri [26]
Fishtine [7] @ T_b						Watson [31,32]
Hydrocarbons (30)	0.70	1.43	0.75			
Nonhydrocarbons (51)	1.64	1.68	1.99			
Inorganics (12)	0.45	2.43	1.48			
All compounds (93)	1.29	1.70	1.52			
Chen [4]						
All compounds (165) @ T_b	1.85	2.40	2.02	1.82		2.18
All compounds (12) $T \neq T_b$				2.55		
Haggenmacher [12]						
Hydrocarbons (17) at several temperatures					~ 1.0	
Viswanath and Kuloor [29] @ T_b						
All compounds (51)		2.20	2.27			
Sastri <i>et al.</i> [26] @ T_b						
Hydrocarbons (42)	1.10	2.30	1.10	0.80		1.00
Nonhydrocarbons (33)	2.10	2.10	2.10	2.10		2.40
All compounds (75)	1.60	2.20	1.50	1.40		1.60

a. Values in parentheses are number of compounds tested.

b. Input parameters for all estimations were known.

where

- dP/dT = derivative of the vapor pressure with respect to temperature
 ΔH_v = heat of vaporization at temperature T
 V_g = saturated molal volume of the vapor phase
 V_l = saturated molal volume of the liquid phase

The quantity $(V_g - V_l)$ can be obtained from the compressibility-factor equation of state [1]:

$$V_g - V_l = \frac{RT}{P} (Z_g - Z_l) \quad (13-2)$$

where R is the universal gas constant and Z_g and Z_l are the compressibility factors for the vapor and the liquid phases respectively. Substitution of Eq. 13-2 into the Clapeyron equation and rearrangement yields the following:

$$\frac{d(\ln P)}{d(1/T)} = \frac{-\Delta H_v}{R(Z_g - Z_l)} \quad (13-3)$$

This equation is frequently the starting point for methods of estimating the heat of vaporization of a material or predicting the shape of its vapor pressure curve.

The Klein method utilizes T_b , T_c , and P_c to estimate heats of vaporization. Starting with Eq. 13-3 and assuming that the right side of this equation is constant, the Klein equation is obtained by integrating Eq. 13-3 between the limits of T_b , 1 and T_c , P_c . When he found that this method often underestimated ΔH_v , Fishtine [8] introduced an empirical correction factor, K_{kl} , whose value is a function of T_b (see Table 13-3). The modified Klein equation that resulted is

$$\Delta H_{vb} = R K_{kl} T_b \frac{(\ln P_c) \sqrt{1 - 1/[(P_c)(T_b/T_c)^3]}}{1 - (T_b/T_c)} \quad (13-4)$$

where R is 1.9872 cal/K-mol, ΔH_{vb} is in units of cal/mol, P_c is in atmospheres, and T_b and T_c are in K. The square root term represents an estimate of the quantity $Z_g - Z_l$ in Eq. 13-3.

The Giacalone method was derived from Eq. 13-3 in a similar manner. Rather than estimating a value for the compressibility differences

TABLE 13-3

Values for Klein Constant

T_b (K)	K_{kl}
< 200	1.02
200-300	1.04
> 300	1.045

Source: Fishtine [8]

$Z_g - Z_l$, Giacalone proposed use of the value 1. This is a reasonable approximation for values near the boiling point: $Z_g - Z_l$ ranges from 0.95 at T_b to 1.00 at $0.74 T_b$. With this assumption, Eq. 13-3 becomes:

$$\Delta H_{vb} = \frac{R T_b \ln(P_c)}{1 - (T_b/T_c)} \quad (13-5)$$

This equation is most accurate for nonhydrocarbons and polar organic compounds, but it can be used for many kinds of compounds.

The Riedel equation is an empirically derived relation for estimating ΔH_{vb} for nonpolar or slightly polar organic compounds. Riedel started with an equation similar to Eq. 13-5 and performed a two-parameter fit to data from nonpolar and slightly polar organic compounds to obtain:

$$\Delta H_{vb} = \frac{T_b (5 \log P_c - 2.17)}{0.930 - (T_b/T_c)} \quad (13-6)$$

where 0.930 and 2.17 are the best-fit values from the parameter fitting. As with the Giacalone method, the Riedel method can give reasonably accurate results for compound types other than those for which it was developed.

The final method that uses T_b , T_c , and P_c to estimate ΔH_{vb} is the empirical method of Chen, who graphically and numerically correlated the heat of vaporization with these three parameters using Pitzer's correlation [22]. (Pitzer tabulated sets of values for predicting the entropy of vaporization at reduced temperatures.) By applying thermodynamic considerations to the work of Pitzer, Chen obtained a linear equation relating the logarithm of the reduced pressure to the ratio between the heat of

vaporization and temperature. When this equation was subjected to linear regression analysis for heats of vaporization at the normal boiling point, the following result was obtained:²

$$\Delta H_{vb} = \frac{T_b [7.11 \log P_c - 7.82 + 7.9 (T_b/T_c)]}{1.07 - (T_b/T_c)} \quad (13-7)$$

To estimate the heat of vaporization at the normal boiling point by any of the preceding four equations, one must have either measured or estimated values of T_b , T_c , and P_c . Methods for estimating T_b and T_c are described in Chapter 12. The critical pressure, P_c , may be estimated by methods analogous to those given in §12-4 of that chapter.

Lydersen proposed a simple additive atomic group contribution method for estimating P_c with the following equation:

$$P_c = \frac{M}{(0.34 + \Sigma \Delta P)^2} \quad (13-8)$$

where P_c is in atmospheres and M is the molecular weight in grams per mole. $\Sigma \Delta P$ is a dimensionless number found by summing the increments listed in Table 13-4 for each atomic and structural feature of the compound of interest.

Another method for estimating P_c , proposed by Forman and Thodos, is based on correlation of P_c with Van der Waal's constants "a" and "b." These parameters, which can be estimated by the procedures described in §12-4 of Chapter 12, are substituted into Eq. 13-9 to determine the value of P_c in atmospheres.

$$P_c = \frac{a}{27 b^2} \quad (13-9)$$

Basic Steps

- (1) Obtain T_b and T_c from the literature, or estimate them by methods in Chapter 12.
- (2) Obtain P_c from literature, or estimate it using Eq. 13-8 or 13-9.
- (3) Find H_{vb} by substituting the above values in one of the following equations:
 - Eq. 13-4 (generally applicable)
 - Eq. 13-5 (nonhydrocarbon polar organic compounds)

2. To use Chen's method for $T \neq T_b$, substitute T for T_b and P_c/P for P_c .

TABLE 13-4

Lydersen's Critical Pressure Increments

- There are no increments for hydrogen.
- All bonds shown as free are connected to atoms other than hydrogen.
- Values in parentheses may be subject to large errors.

Atomic Group	ΔP	Atomic Group	ΔP
Nonring Increments		Oxygen Increments (cont.)	
$-\text{CH}_3$	0.227	$-\text{O}-$ (nonring)	0.16
$-\overset{ }{\text{CH}_2}$	0.227	$-\text{O}-$ (ring)	(0.12)
$-\overset{ }{\text{CH}}$	0.210	$-\overset{ }{\text{C}}=\text{O}$ (nonring)	0.29
$\diagup \text{C} \diagdown$	0.210	$-\overset{ }{\text{C}}=\text{O}$ (ring)	(0.2)
$=\text{CH}_2$	0.198	$\text{HC}=\text{O}$ (aldehyde)	0.33
$=\overset{ }{\text{C}}-$	0.198	$-\text{COOH}$ (acid)	(0.4)
$=\text{C}=\text{C}=\text{C}$	0.198	$-\text{COO}-$ (ester)	0.47
$\equiv\text{CH}$	0.153	$=\text{O}$ (except for above combinations)	(0.12)
$\equiv\text{C}-$	0.153		
Ring Increments		Nitrogen Increments	
$-\text{CH}_2-$	0.184	$-\text{NH}$	0.095
$-\overset{ }{\text{CH}}$	0.192	$-\overset{ }{\text{NH}}$ (nonring)	0.135
$\diagup \text{C} \diagdown$	(0.154)	$-\overset{ }{\text{NH}}$ (ring)	(0.09)
$=\overset{ }{\text{CH}}$	0.154	$-\overset{ }{\text{N}}-$ (nonring)	0.17
$=\overset{ }{\text{C}}-$	0.154	$-\overset{ }{\text{N}}-$ (ring)	(0.13)
$=\text{C}=\text{C}=\text{C}$	0.154	$-\text{CN}$	(0.36)
Halogen Increments		$-\text{NO}_2$	(0.42)
$-\text{F}$	0.224	Sulfur Increments	
$-\text{Cl}$	0.320	$-\text{SH}$	0.27
$-\text{Br}$	(0.50)	$-\text{S}-$ (nonring)	0.27
$-\text{I}$	(0.83)	$-\text{S}-$ (ring)	(0.24)
Oxygen Increments		$=\text{S}$	(0.24)
$-\text{OH}$ (alcohols)	0.06	Miscellaneous	
$-\text{OH}$ (phenols)	(-0.02)	$-\overset{ }{\text{Si}}-$	(0.54)

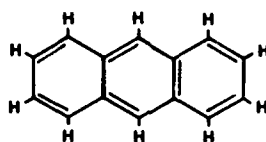
Source: Lydersen [14b]; also tabulated in Reid and Sherwood [24]

- Eq. 13-6 (nonpolar or slightly polar organic compounds)
- Eq. 13-7 (generally applicable)

Example 13-1 Estimate ΔH_{vb} for anthracene, assuming that no measured values of the input parameters are available.

- (1) Using the methods described in § 12-4, the estimated values of T_c and T_b are 880.6K and 614K respectively. (See Example 12-4 for details of this calculation.)
- (2) Estimate P_c as follows:

- Sketch the structure of anthracene



- Refer to Table 13-4 and add the ΔP contributions for the component atomic groups in anthracene.

$$(10) \quad \text{H}-\overset{|}{\text{C}}= = 10(0.154) = 1.54$$

$$(4) \quad -\overset{|}{\text{C}}= = 4(0.154) = 0.62$$

$$\Sigma \Delta P = 2.16$$

- Substitute $\Sigma \Delta P$ in Eq. 13-8. (The molecular weight of anthracene is 178.3 g.)

$$P_c = \frac{178.3}{(0.34 + 2.16)^2}$$

$$= 28.5 \text{ atm}$$

- (3) Calculate ΔH_{vb} from the values estimated above. Using the modified Klein method,

- $K_{k1} = 1.045$ from Table 13-3.

- Substituting in Eq. 13-4,

$$\Delta H_{vb} = 1.987(1.045)(614) \frac{\ln(28.5) \sqrt{1 - 1/[(28.5)(614/880.6)^3]}}{1 - (614/880.6)}$$

$$= 13,400 \text{ cal/mol}$$

Since the measured ΔH_{vb} is 13,500 cal/mol, the relative error is -0.74%.

- (4) If the Giacalone method (Eq. 13-5) is used,

$$\begin{aligned}\Delta H_{vb} &= \frac{(1.987)(614) \ln(28.5)}{1 - (614/880.6)} \\ &= 13,500 \text{ cal/mol, which agrees with the measured value} \\ &\quad \text{within the accuracy of the calculation.}\end{aligned}$$

- (5) By the Riedel method (Eq. 13-6),

$$\begin{aligned}\Delta H_{vb} &= \frac{(614) [5 \log(28.5) - 2.17]}{0.930 - (614/880.6)} \\ &= 13,500 \text{ cal/mol, which again agrees with the measured} \\ &\quad \text{value.}\end{aligned}$$

- (6) Using the Chen method (Eq. 13-7),

$$\begin{aligned}\Delta H_{vb} &= \frac{(614) [7.11 \log(28.5) - 7.82 + 7.9 (614/880.6)]}{1.07 - (614/880.6)} \\ &= 13,230 \text{ cal/mol, which deviates } -2.0\% \text{ from the measured} \\ &\quad \text{value.}\end{aligned}$$

13-5 ESTIMATION OF ΔH_{vb} FROM VAPOR PRESSURE DATA

Principles of Use. Equation 13-3 describes the shape of the vapor pressure curve for any material as a function of the heat of vaporization and the difference in the compressibility factors for the liquid and the vapor phases. The shape of the vapor pressure curve may also be described by Antoine's relationship:

$$\log P = A - \frac{B}{t + C} \quad (13-10)$$

where A, B, and C are constants and t is the temperature, all expressed in °C except A, which is dimensionless. Haggmacher [11,12] combined Eq. 13-10 with Eq. 13-3 and Eq. 13-11, which expresses the compressibility difference in terms of two pressures and two temperatures:

$$Z_g - Z_l = \sqrt{1 - (P/P_c)/(T/T_c)^3} \quad (13-11)$$

This resulted in the following expression:

$$\Delta H_v = \frac{2.303BRT^2 \sqrt{1 - (P/P_c)/(T/T_c)^3}}{(t + C)^2} \quad (13-12)$$

where T and T_c are in K, P and P_c are in atmospheres, and B , C , and t are in $^{\circ}\text{C}$. The constant 2.303 is the natural logarithm of 10, and R is equal to 1.9872 cal/K-mol. At the normal boiling point (where $T = T_b$, $t = t_b$, and $P = 1$ atm), Eq. 13-12 becomes

$$\Delta H_{vb} = \frac{2.303 B R T_b^2 \sqrt{1 - (1/P_c)/(T_b/T_c)^3}}{(t_b + C)^2} \quad (13-13)$$

where T_b and T_c are in K, P_c is in atmospheres, and B , C , and t_b are in $^{\circ}\text{C}$. T_b , T_c , and t_b may be estimated from the methods of Chapter 12, and P_c may be estimated by one of the two procedures outlined in §13-4 of this chapter.

Antoine's constants (A, B, C) have been calculated for many compounds, especially hydrocarbons, and are tabulated in the literature [23,34]. For compounds whose Antoine's constants are not readily available, C may be estimated if the normal boiling point is known; Table 13-5 summarizes the estimation procedure for organic or organometallic compounds. Linear interpolation should be used to estimate C for boiling points that fall between the values listed.

TABLE 13-5

Antoine's Constant C for Organic Compounds

Polyhydric Alcohols (diols, triols, etc.): $C = 230^{\circ}\text{C}$

Other Organic and Organometallic Compounds:

Boiling Pt. ($^{\circ}\text{C}$)	C ($^{\circ}\text{C}$)	Boiling Pt. ($^{\circ}\text{C}$)	C ($^{\circ}\text{C}$)
< -150	$264 - 0.034 t_b$	140	212
-150 to -10	$240 - 0.19 t_b$	160	206
-10	238	180	200
0	237	200	195
20	235	220	189
40	232	240	183
60	228	260	177
80	225	280	171
100	221	> 300	165
120	217		

Source: Fishtine [9]

Antoine's constant B can be estimated from the value of C and two vapor pressure-temperature pairs:

$$B = \frac{(t_2 + C)(t_1 + C)}{t_2 - t_1} \log(P_2/P_1) \quad (13-14)$$

Although any two pairs of temperatures and corresponding vapor pressures may be substituted in this equation, Fishtine [9] determined that the boiling points at pressures of 760 mm Hg (1 atm) and 10 mm Hg (0.013 atm) give the most reliable estimates of B, typically within 1%. Since t at 760 mm Hg is the normal boiling point, Eq. 13-14 becomes

$$B = \frac{(t_b + C)(t_{10} + C)}{t_b - t_{10}} (1.881) \quad (13-15)$$

where B, C, t_b , and t_{10} are in °C, t_{10} is the temperature corresponding to 10 mm Hg vapor pressure, and $1.881 = \log(760/10)$.

Most tabulations express Antoine's constants in degrees Celsius, but some (such as in Reid *et al.* [31]) use the Kelvin scale. The constant C is converted to Celsius degrees in the usual way (i.e., by subtracting 273.16), but the value of B *should not be changed*; this is because B represents the slope of the curve that relates ΔH_v to temperature, and the slope is not affected by a change from Kelvin to Celsius.

Care should also be taken to establish whether the listed values of B include a factor of 2.303 for converting from base-10 to base-e logarithms. Most tabulations of Antoine's constants list values of B calculated from equations such as 13-14 or 13-15, which use the common logarithm of the pressure ratio; however, some tabulations, such as those of Reid, include in the value of B the conversion factor to natural log. A simple method for determining whether this has been done is to check the value for methane, which is likely to be listed in any tabulation of Antoine's constants. If it is 405.42 (°C or K), the listed values may be used directly in the preceding equations; if it is about 930°, the B values have been multiplied by 2.303.

If T_c and P_c are not known and cannot be estimated, the difference in the compressibility factors ($Z_g - Z_l$) may be obtained from Table 13-6; the error associated with this approximation is usually 2% or less. The

TABLE 13-6

Estimation of Compressibility-Factor
Difference from Temperature

T/T_b^a	$Z_g - Z_l$
1.00	0.95
0.98	0.96
0.94	0.97
0.90	0.98
0.84	0.99
0.74	1.00

a. Note that both temperatures must be expressed in K.

Source: Fishtine [9]

result is then substituted into the following equation, which is equivalent to Eq. 13-13:

$$\Delta H_{vb} = \frac{2.303 B R T_b^2 (Z_g - Z_l)}{(t_b + C)^2} \quad (13-16)$$

Basic Steps

- (1) Obtain the values of T_b and T_c from the literature, or estimate them by the methods given in Chapter 12.
- (2) Obtain the value of P_c from the literature, or estimate it by the methods given in §13-4 of this chapter.
- (3) Obtain Antoine's constants B and C from the literature, or estimate C from Table 13-5 and B from Eq. 13-15 (in °C).
- (4a) Substitute T_b , T_c , P_c , B, and C into Eq. 13-13 to estimate ΔH_{vb} (in cal/mol) if T_c and P_c are known.
- (4b) If T_c and/or P_c is not available and cannot be estimated, find the appropriate value of $Z_g - Z_l$ in Table 13-6.
- (5) Substitute T_b , B, C, and $Z_g - Z_l$ into Eq. 13-16 to estimate ΔH_{vb} (in cal/mol).

Example 13-2 Estimate ΔH_{vb} for methyl benzoate using Eqs. 13-13 and 13-16, given $T_b = 472.2\text{K}$, $T_c = 692\text{K}$, and $P_c = 36\text{ atm}$. (The measured value of ΔH_{vb} is 10,300 cal/mol.)

- (1) From Table 13-6,

$$Z_g - Z_l = 0.95$$

From Ref. 34,

$$C = -81.15\text{K}$$

$$B = 3751.83\text{K}$$

The Celsius equivalents are

$$C = 192.01^\circ\text{C}$$

$$B = 3751.83^\circ\text{C}$$

For methane, this reference lists $B = 897.84\text{K}$, which indicates that the values listed are actually $2.303B$.

- (2) Compute ΔH_{vb} from Eq. 13-13.

$$\begin{aligned}\Delta H_{vb} &= \frac{3751.83 (1.9872) (472.2)^2 \sqrt{1 - [(1/36)/(472.2/692)^3]}}{[(472.2 - 273.2) + 192.01]^2} \\ &= 10,400 \text{ cal/mol}\end{aligned}$$

The deviation from the measured ΔH_{vb} is 100 cal/mol, indicating a relative error of +1.0%.

- (3) To compute ΔH_{vb} from Eq. 13-16, the value of $Z_g - Z_l$ is needed. Since $T/T_b = 1$ at the boiling point, $Z_g - Z_l = 0.95$ (Table 13-6). This value will limit the accuracy of the calculation to two significant figures.

- (4) Substituting in Eq. 13-16,

$$\begin{aligned}\Delta H_{vb} &= \frac{(3751.83) (1.9872) (472.2)^2 (0.95)}{[(472.2 - 273.2) + 192.01]^2} \\ &= 10,000 \text{ cal/mol, which deviates from the measured value by } -3\%.\end{aligned}$$

13-6 ESTIMATION OF ΔH_{vb} FROM COMPOUND STRUCTURE

Principles of Use. Sastri and coworkers [26] have developed a method for estimating ΔH_{vb} for any organic compound from its molecular structure. This method is based on previous work by Bowden and Jones [3] and by others listed in Ref. 26; these researchers attempted to develop a series of structural constants similar to the parachor but which would be temperature-independent and thereby useful for predicting various thermodynamic properties from the structure of a compound.

The relationship between the heat of vaporization of a compound and the sum of its structural increments is defined by Sastri as

$$\Delta H_{vb} = H_{vo} (1 - T_b/T_c)^n \quad (13-17)$$

where H_{vo} is the sum of the structural increments for the heat of vaporization and the constant n is a function of the ratio T_b/T_c (see Table 13-7), which frequently has a value between 0.37 and 0.38.

TABLE 13-7

Values of Exponent n as a Function of T_b/T_c

T_b/T_c	n
< 0.57	0.30
0.57-0.71	$0.74(T_b/T_c) - 0.116$
> 0.71	0.41

Source: Fishtine, as cited by Reid *et al.* [24]

The ratio of T_b to T_c may be estimated by the Lydersen method (see §12-4 in the preceding chapter) if either T_b or T_c is unknown. For those cases where the Lydersen method cannot be used, the early work of Guldberg (referenced in [24]) showed that $T_b/T_c \approx 2/3$ for most organic compounds, and this value may be inserted into Eq. 13-17.

The value of H_{vo} is found by summing the increments for each atom or functional group in the molecule. Table 13-8 lists the increments for atoms and functional groups containing C, H, N, O, S, and the halogens. Note that the increments are listed in units of kilocalories, so the resulting value of H_{vo} must be multiplied by 1000 to express it in cal/mol. The values for the halogen atoms vary with the compound structure, and Table 13-9 lists rules to follow for selecting the proper increment. Table 13-10 lists correction increments for three specific compound types, predominantly small or polar organic compounds.

Basic Steps

- (1) Draw the structure.
- (2) Obtain T_b and T_c from the literature or estimate T_b/T_c by Lydersen's method (Eq. 12-5) or use $T_b/T_c = 2/3$.
- (3) Obtain exponent n from Table 13-7.

TABLE 13-8
Structural Group Increments for H_{vo}

Group	Increment (kcal/mol)	Group	Increment (kcal/mol)	Group	Increment (kcal/mol)
Aliphatic and Alicyclic Hydrocarbons		Aromatic Hydrocarbons		Sulfur Increments	
-H	0.20	$\text{CH}-$	1.68	-SH	4.65
-CH ₂	2.38	$=\text{C}-$	0.76	-S-	3.50
-CH ₂ -	1.44	$=\text{C}'$	1.20	Nitrogen Increments	
-CH-	0.08	(Bridge carbon in condensed ring system)		-C≡N	7.65
$\text{C}-$	-1.62	Hydrocarbon Structures, Nonsaromatic		-NH ₂	5.60
=CH ₂	2.19	3-membered ring	2.20	NH	3.00 (aliphatics) 4.10 (aromatics) 4.10 (heterocyclics)
=CH-	1.50	4-membered ring	2.55	$\text{N}-$	0.30 (aliphatics) 1.75 (aromatics) 3.00 (heterocyclics)
$\text{C}-$	0.19	5-membered ring	1.85	-NO ₂	8.60 (aliphatics) 5.70 (aromatics)
=C=	1.85	5-membered ring and monoalkene	1.60		
≡CH	2.35	6-membered ring	1.50		
≡C-	2.00	6-membered ring and alkene	1.55		

(Continued)

TABLE 13-8 (Continued)

Group	Increment (kcal/mol)	Group	Increment (kcal/mol)	Group	Increment (kcal/mol)
Oxygen Increments					
-OH	9.80 (alcohols, primary bonded)	$\begin{array}{c} \text{H} \\ \\ -\text{C}=\text{O} \\ \\ \diagup \text{C}=\text{O} \\ \end{array}$	Oxygen Increments (cont.) 5.70 4.40 (aliphatics) 2.80 (aromatics) 12.50 (acids with ≤ 10 C atoms) 6.70 (acids with > 10 C atoms) 4.20 (esters with ≤ 8 C atoms) 3.00 (esters with > 8 C atoms)	Halogen Increments^a -F -Cl -Br -I	2.50 (A types) 1.00 (B types) 1.75 (aromatics) 4.10 (A types) 2.60 (B types) 3.10 (aromatics) 4.60 (A types) 3.60 (B types) 3.60 (aromatics) 6.00 (A types) 5.00 (B types) 5.00 (aromatics)
	9.00 (monohydroxy alcohols, secondary and tertiary bonded)				
	8.60 (dihydroxy alcohols, secondary and tertiary bonded)				
	3.80 (trihydroxy alcohols, secondary and tertiary bonded)				
	6.40 (phenols)				
-O-	2.05 (ethers)	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}- \end{array}$			
	0.80 (aliphatics containing nonhydrocarbon groups other than halogens)				
	2.90 (heterocyclics)				

a. See Table 13-9 for definitions of types A and B.
Source: Sastri, *et al.* [26].

TABLE 13-9
Rules for Using Type A or Type B Halogen Increments

Compound	Increment Type
Monohalogenated Aliphatics	
Halogen attached to hydrocarbon group (e.g., CH ₃ Cl)	A
Halogen attached to nonhydrocarbon group (e.g., CH ₃ COCl or CH ₃ COOCi)	B
Multihalogenated Aliphatics	
Saturated compounds with x carbons	A for $\leq x$ halogens B for $> x$ halogens
Unsaturated compounds with x carbons	A for $\leq x-1$ halogens B for $> x-1$ halogens
Exceptions	
Both halogens in methylene compounds	A
For compounds containing more than one type of halogen, assign type-A increments starting with lowest atomic number halogen until x halogens (if saturated) or x-1 halogens (if unsaturated) have been assigned. Use type-B increments for any additional halogens (e.g., C ₂ FCl ₅ has 1 type-A F, 1 type-A Cl, and 4 type-B Cl)	

Source: Sastri, *et al.* [26].

- (4) Obtain and sum H_{vo} increments from Tables 13-8 to 13-10.
- (5) Estimate ΔH_{vb} (in cal/mol) from Eq. 13-17.

Example 13-3 Estimate ΔH_{vb} for anthracene by the Sastri method. (The measured value of ΔH_{vb} is 13,500 cal/mol.)

- (1) The structure of anthracene is

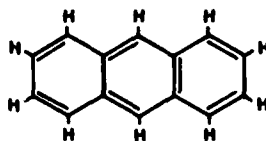


TABLE 13-10

Correction Increments

Compound	Correction Increment (kcal/mol)
Aliphatic compounds (not esters) with single nonhydrocarbon group attached to $-\text{CH}_3$, methyl group (e.g., CH_3Cl , $\text{CH}_3\text{N}(\text{CH}_3)_2$)	0.60 ^a
Aliphatic compounds formed by the addition of $-\text{H}$, single hydrocarbon to the nonhydrocarbon group; includes esters of formic acid (e.g., CH_3COOH)	1.85 ^a
Esters with $-\text{CH}_3$ attached to $-\text{COO}-$	0.90 ^b

a. No correction required if compound is associated in the gas phase (e.g., CH_3COOH , HCOOH).

b. Increment added for each $-\text{CH}_3$ attached to $-\text{COO}-$ group; thus, methyl acetate ($\text{CH}_3\text{COOCH}_3$) would have correction of 2×0.90 .

Formate esters such as HCOOCH_3 would have increments of $0.90 + 1.85$.

Source: Sastri, *et al.* [26]

(2) From the literature,

$$T_b = 614.4\text{K}$$

$$T_c = 883\text{K}$$

$$T_b/T_c = 0.6958$$

(3) From Table 13-7,

$$n = 0.40$$

(4) From Table 13-8,

Structure	Number	Increment	
$=\text{C}'$ aromatic	4	$\times 1.20$	$= 4.80$
$=\text{CH}-$ aromatic	10	$\times 1.68$	$= 16.80$
		ΣH_{vo}	$= 21.60$

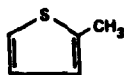
- (5) Compute H_{vb} from Eq. 13-17:

$$\begin{aligned}\Delta H_{vb} &= 21.60(1 - 614.4/883)^{0.40} \\ &= 13 \text{ kcal/mol} \\ &= 13,000 \text{ cal/mol}\end{aligned}$$

This result is accurate to only two significant figures because of n ; compared with the measured value (rounded off to 14,000 cal/mol), it shows a deviation of -7%.

Example 13-4 Compute ΔH_{vb} for 2-methylthiophene using the Sastri method. (The measured value of ΔH_{vb} is 8103 cal/mol.)

- (1) The structure of 2-methylthiophene is



- (2) Using Lydersen's method, Table 12-6 gives the following ΔT increments:

Group	Number	Increment
$-\text{CH}_3$	1	$\times 0.020 = 0.020$
$=\text{CH}-$ ring	3	$\times 0.011 = 0.033$
$=\overset{ }{\text{C}}-$ ring	1	$\times 0.011 = 0.011$
$-\text{S}-$ ring	1	$\times 0.008 = 0.008$
		$\Sigma \Delta T = 0.072$

Then, by Eq. 12-5,

$$\begin{aligned}\theta &= T_b/T_c = 0.567 + \Sigma \Delta T - (\Sigma \Delta T)^2 \\ &= 0.567 + 0.072 - (0.072)^2 \\ &= 0.634\end{aligned}$$

- (3) From Table 13-7, $n = 0.353$

- (4) From Table 13-8,

Group	Number	Increment
$-\text{CH}_3$	1	$\times 2.38 = 2.38$
$=\text{CH}-$ ring	3	$\times 1.68 = 5.04$
$=\overset{ }{\text{C}}-$ ring	1	$\times 0.76 = 0.76$
$-\text{S}-$	1	$\times 3.50 = 3.50$
		$\Sigma H_{vo} = 11.68$

(5) From Eq. 13-17:

$$\begin{aligned}\Delta H_{vb} &= 11.68 (1 - 0.634)^{0.353} \\ &= 8.19 \text{ kcal/mol} \\ &= 8,190 \text{ cal/mol, which deviates from the measured value} \\ &\quad \text{by +1.1\%}.\end{aligned}$$

13-7 ESTIMATION OF ΔH_v AT TEMPERATURES OTHER THAN THE BOILING POINT

The previous methods of this chapter permitted estimation of the heat of vaporization at the normal boiling point. Although this is sufficient for most applications, the value of ΔH_v at other temperatures is sometimes needed. The Thiesen correlation [7] is frequently used as a starting point:

$$\Delta H_v = k(1 - T/T_c)^n \quad (13-18)$$

where k and n are constants, ΔH_v is the heat of vaporization at temperature T , and T_c is the critical temperature. If k , n and T_c are known for a compound, ΔH_v can be computed for any temperature T . Values of k and n have been calculated for some compounds, but most of the methods based on Eq. 13-18 form the ratio of this equation at two temperatures, as shown below.

$$\frac{\Delta H_{v2}}{\Delta H_{v1}} = \left[\frac{(1 - T_2/T_c)}{(1 - T_1/T_c)} \right]^n \quad (13-19)$$

or

$$\Delta H_{v2} = \Delta H_{v1} \left[\frac{(1 - T_2/T_c)}{(1 - T_1/T_c)} \right]^n \quad (13-20)$$

where ΔH_{v1} and ΔH_{v2} are the heats of vaporization at temperatures T_1 and T_2 , respectively. With Eq. 13-20, the heat of vaporization at any temperature may be estimated as long as one other heat of vaporization is known. It is convenient to choose the normal boiling point as one of the temperatures, since the heat of vaporization at the normal boiling point is either known or may be estimated by the methods presented earlier in this chapter. Therefore, Eq. 13-21 is normally used for estimating the heat of vaporization at any temperature other than the normal boiling point.

$$\Delta H_v = \Delta H_{vb} \left[\frac{(1 - T/T_c)}{(1 - T_b/T_c)} \right]^n \quad (13-21)$$

Various values have been used for n . The most common is 0.38, which was proposed by Watson [32] and yields estimates typically within 2%. Fishtine (in Ref. 24) has proposed a correlation of n with the ratio of T_b/T_c , which yields better estimates of ΔH_v ; this correlation is summarized in Table 13-7, and corresponding values of n should be used in Eqs. 13-19, -20, and -21.

Basic Steps

- (1) Obtain T_b/T_c from the literature, or estimate it by the methods of Chapter 12.
- (2) Obtain ΔH_{vb} from the literature, or estimate it as described in §13-3, §13-4, or §13-5.
- (3) Obtain n from Table 13-7.
- (4) Compute ΔH_v at temperature T from Eq. 13-21.

Example 13-5 Estimate the heat of vaporization for isooctane at 25°C, given $T_b = 372.4\text{K}$ and $T_c = 543.9\text{K}$. (The measured value is 8,397 cal/mol.)

- (1) $T_b/T_c = 0.6847$
- (2) From the literature [34]:

$$\Delta H_{vb} = 7.411 \text{ kcal/mol}$$

- (3) From Table 13-7:

$$\begin{aligned} n &= 0.74(0.6847) - 0.116 \\ &= 0.39 \end{aligned}$$

- (4) Compute ΔH_v from Eq. 13-21:

$$\begin{aligned} \Delta H_v &= 7.411 \left[\frac{1 - (298/543.9)}{1 - 0.6847} \right]^{0.39} \\ &= 8.5 \text{ kcal/mol} \\ &= 8,500 \text{ cal/mol, which deviates from the measured value by +1.2\%.} \end{aligned}$$

13-8 AVAILABLE DATA

Data on heats of vaporization are available from many sources. The values listed may be measured at a temperature of 25°C or at the normal boiling point. In addition to the general references listed in Appendix A, the following are recommended:

Dean, J.A. [6] — General data, including heats of vaporization for inorganic and organic compounds.

Reid, R.C. *et al.* [23] — Appendix tabulates heats of vaporization and Antoine's constants for many organic compounds.

Perry, R.H. and C.H. Chilton [21] — General chemical engineering information, including heats of vaporization for organic and inorganic compounds.

Zwolinski, B.J. and R.C. Wilhoit [34] — Vapor pressures and heats of vaporization for hydrocarbons and related compounds.

Washburn, E.E. [30] — Critical constants and heats of vaporization for numerous compounds.

Thakore, S.B. *et al.* [27b] — Correlation constants for the Watson relationship (Eq. 13-20) for many common chemicals.

13-9 SYMBOLS USED

a, b	=	Van der Waal's constants in Eq. 13-9
A, B, C	=	Antoine's constants in Eq. 13-10
ΔH_v	=	heat of vaporization at temperature T (cal/mol)
H_{vo}	=	sum of Sastri heat of vaporization structural increments in Eq. 13-17 (kcal/mol)
k	=	constant in Eq. 13-18
K_{kl}	=	Klein constant in Eq. 13-4
M	=	molecular weight in Eq. 13-8 (g/mol)
n	=	exponent in Eqs. 13-17 to 13-21
ΔP	=	Lydersen increment for estimation of P_c in Eq. 13-8
P	=	vapor pressure (atm)
R	=	universal gas constant = 1.9872 cal/mol
t	=	temperature (°C)
t_{10}	=	temperature corresponding to a vapor pressure of 10 mm Hg in Eq. 13-15 (°C)

- T = temperature (K)
 V = molal volume in Eqs. 13-1 and -2
 Z = compressibility factor in Eqs. 13-2, -3, and -18

Subscripts

- 1 = temperature T_1
 2 = temperature T_2
 b = boiling point
 c = critical property
 g = vapor phase
 l = liquid phase

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14

VAPOR PRESSURE

Clark F. Grain

14-1 INTRODUCTION

Reliable methods for estimating the vapor pressures of organic materials are of increasing importance as a tool in predicting the behavior and fate of chemicals that are introduced into the environment. When a chemical has been spilled, for example, we must know its approximate vapor pressure in order to estimate its rate of evaporation. The persistence of insecticides, herbicides, and similar substances that have been absorbed in the soil is also highly dependent on this chemical-specific property.

Numerous equations and correlations for estimating vapor pressure are presented in the literature. In general, they require information on at least three of the following properties: (1) the critical temperature, T_c , (2) the critical pressure, P_c , (3) the heat of vaporization, ΔH_v , and/or (4) the vapor pressure (P_{vp}) at some reference temperature. For most liquids at room temperature, the vapor pressure ranges from 10^{-6} to 300 millimeters of mercury.

The equations that relate vapor pressure to temperature are commonly derived by integration of the Clausius-Clapeyron equation

$$\frac{d \ln P_{vp}}{dT} = \frac{\Delta H_v}{\Delta Z RT^2} \quad (14-1)$$

where P_{vp} is the vapor pressure in *atmospheres*, ΔH_v is the heat of vaporization in cal/mol, R is the gas constant in cal/mol·K, T is the temperature in K, and ΔZ is a compressibility factor, given by

$$\Delta Z = \frac{P_{vp} \Delta V}{RT} \quad (14-2)$$

where ΔV is the volume difference between vapor and liquid. In Eq. 14-2 R has the units $\text{cm}^3\text{-atm/K}$, hence, ΔZ is dimensionless and has a value of 1 for an ideal gas.

The simplest equation that can result from integration of Eq. 14-1 is

$$\ln P_{vp} = A_1 - B_1/T \quad (14-3)$$

where A_1 and B_1 can be expressed in terms of the parameters in Eq. 14-1. Equation 14-3 is the result obtained when $\Delta H_v/\Delta Z$ is assumed to be constant with changes in temperature; more complex (but more accurate) vapor pressure equations can be derived by assuming an analytical form for the temperature dependence of ΔH_v .

Most of the estimation and correlation methods are designed for *greatest accuracy* between the normal boiling point, T_b , and the critical temperature, T_c . This range is primarily useful to process engineers, who deal with relatively high temperatures. Environmental studies, however, normally involve temperatures below the boiling point, where such methods are less accurate [8,9]; the need here is for reliable estimates of the vapor pressures of a wide variety of liquids and solids at temperatures in the 10-40°C range. A method for estimating very low vapor pressures ($< 1\text{ mm Hg}$) is particularly needed, and the amount of experimental data required must be kept to a minimum.

14-2 SELECTION OF APPROPRIATE METHOD

Evaluation of Parameters. For maximum utility and convenience, any analytical expression that relates vapor pressure to temperature should have as few arbitrary parameters as possible. The general approach that has been used to minimize the number of such parameters is explained below.

Such an expression is first equated to the vapor pressure at the normal boiling point. Since P_{vp} is then equal to one atmosphere, $\ln P_{vp} = 0$. The first derivative of the analytical expression can also be equated to the Clausius-Clapeyron equation at T_b . Thus, in general,

$$\ln P_{vp} \text{ (atm)} = f(T) \quad (14-4)$$

with boundary conditions

$$\ln P_{vp} \Big|_{T=T_b} = 0 = f(T_b) \quad (14-5)$$

and

$$\frac{d \ln P_{vp}}{dT} \Big|_{T=T_b} = \frac{\Delta H_{vb}}{\Delta Z_b R T_b^2} = f'(T_b) \quad (14-6)$$

By means of Eqs. 14-5 and 14-6, a two-parameter equation can be equated directly to ΔH_{vb} and T_b , while a three-parameter equation can be reduced to an equation with only one adjustable parameter. For example, the parameters in Eq. 14-3 can be evaluated to yield

$$\ln P_{vp} \text{ (atm)} = \frac{\Delta H_{vb}}{\Delta Z_b R} \left[\frac{1}{T_b} - \frac{1}{T} \right] \quad (14-7)$$

In general, however, this equation is quite inaccurate at temperatures below T_b and is not recommended.

If an experimental vapor pressure datum is available, one could, in principle, use the general procedure just outlined, providing it is noted that

$$\ln P_{vb} \Big|_{T=T_1} \neq 0 = f(T_1) \quad (14-8)$$

where T_1 is the experimental temperature datum.

Equation 14-7 is now generalized such that

$$\ln P_{vp} = \ln P_1 + \frac{\Delta H_{v1}}{\Delta Z_b R} \left[\frac{1}{T_1} - \frac{1}{T} \right] \quad (14-9)$$

Note that if $T_1 = T_b$ then $\ln P_1 = 0$ and Eq. 14-9 becomes identical to Eq. 14-7.

The value of ΔH_{v1} must be known in order to use Eq. 14-9 at temperatures other than T_1 . If an experimental value is not available, the methods of Chapter 13 may be used to estimate this quantity. Note,

however, that all of the methods presented in Chapter 13 require a knowledge of T_b , the normal boiling point. This means that at least two data points are necessary in order to estimate P_{vp} , whereas Eq. 14-7 requires T_b only. In §14-5, however, a general method of estimating the ratio $\Delta H_{v1}/T_1$ is provided that obviates the necessity for two data points.

Special mention should be made of the problem of estimating the vapor pressures of solids. If a particular vapor pressure equation is extrapolated below the melting point, one obtains the vapor pressure of the supercooled liquid rather than that of the true "crystalline" solid. Generally, the vapor pressure of the solid is considerably lower than that of the supercooled liquid. Mackay [7] has pointed out that the vapor pressure of the solid can be derived from that of the supercooled liquid by applying a correction based upon the assumption that the entropy of fusion is a constant equal to 13.6 cal/mol·K. Thus,¹

$$\ln P_{vp}(s) = \ln P_{vp}(l) + 6.81 (1 - T_m/T) \quad (14-10)$$

where T_m is the melting point in degrees Kelvin. This correction has been used with limited success with one of the methods recommended in this chapter (Method 1). See Table 14-2.

The other method recommended in this chapter (Method 2) contains one adjustable parameter, which has one value applicable to all liquids and three values for solids, depending upon the ratio of the normal boiling point to the temperature of interest. Thus, no correction is needed and only one experimental input is required.

An interesting correlation has been reported by Chiou and Freed [3], who observed a linear relationship between the logarithm of the vapor pressure at 25°C and the logarithm of the octanol-water partition coefficient, K_{ow} .² The relationship was reasonably accurate for five classes of compounds, namely, aromatic hydrocarbons, organo halogens, aliphatic alcohols, aliphatic acids and chlorinated phenols. We do not recommend this method because of its limited applicability with respect to chemical classes and the fact that it is useful at 25°C only. Future development, however, may lead to greater utility for the method.

General Characteristics. Many vapor pressure equations are given in the literature: Partington [10], for example, lists about 56.³ The two

1. Entropy of fusion/ R = 6.81.
2. Estimation methods for this parameter are provided in Chapter 1.
3. The literature was reviewed in 1965 by Miller [8] and more recently by Reid, Prausnitz, and Sherwood [12]. Additional information is given in Ref. 11.

methods recommended in this chapter require a minimum of experimental data and are applicable to almost any organic material over a wide pressure range. Their accuracy is quite good over the temperature range of interest to environmental scientists.

Basic information on the two methods is summarized in Table 14-1. Note that a choice may be required, depending upon (1) the physical state of the pure material at the temperature and pressure in question, (2) the value of P_{vp} , and (3) the available input data (i.e., whether T_b or some other temperature datum is available).

TABLE 14-1
Recommended Methods

	Method 1		Method 2		
Basis	Antoine Equation [1]		Modified Watson Correlation [17]		
Applicable for:					
Physical State	Liquids and Gases		Liquids and Solids		
Range of P_{vp} (mm Hg)	10^{-3} –760		10^{-7} –760		
Input Required ^a	T_b		T_b		
Method Error (%) ^b	2.7	86.3	2.5	38.7	46.9
for P_{vp} Range (mm Hg) of	10–760	10^{-3} –10	10–760	10^{-3} –10	10^{-7} – 10^{-3}

a. If a boiling point (T_b) at some reduced pressure (P_r) is available, this information may be used in place of T_b . Instructions are provided in §14-5.

b. From Table 14-3.

In Table 14-2, vapor pressures calculated by both methods are compared with experimental values for a wide variety of materials. The only experimental data required for either method is the normal boiling point, T_b . If T_b is unavailable, it can be estimated by one of the methods described in Chapter 12.

Method 1 is generally applicable over the pressure range from 760 mm to 10^{-3} mm. Method 2 is applicable from 760 mm to at least 10^{-7} mm. Reid *et al.* [12] state that none of the vapor pressure equations are suitable for estimating pressures below 10 mm within a 10% deviation from experimental data. In many instances, however, particularly for compounds of environmental concern, such a stringent requirement is unnecessary; in estimating the volatilization of a chemical from an open

TABLE 14-2

Calculated vs Experimental Vapor Pressures

Material	T_b (K)	t ($^{\circ}\text{C}$)	Experimental P_{vp} (mm) ^a	Calculated P_{vp} (mm)	
				Method 1	Method 2
Liquids and Solids using Experimental T_b Data					
Acetone	329	30(l)	270	278	272
Hexane	342	20(l)	120	124	121
Benzene	353	20(l)	76	81	76
Ethanol	351	20(l)	43	45	41
1,4-Dioxane	374	20(l)	30	32	29
2-Ethyl-butylaldehyde	390	20(l)	14	14	13
Acetic acid	391	20(l)	14	14	13
Chloroethanol	402	20(l)	5	3	3
Allyl glycidyl ether	427	20(l)	4	3	3
Furfural	435	20(l)	1	2	1
Aniline	457	20(l)	3×10^{-1}	5×10^{-1}	5×10^{-1}
Phenol	455	20(s)	2×10^{-1}	4×10^{-1}	2×10^{-1}
p-Chloroaniline	505	20(s)	2×10^{-2}	1×10^{-2}	2×10^{-2}
Ethylene glycol	471	20(l)	2×10^{-2}	4×10^{-2}	4×10^{-2}
Glycerol	564	50(l)	3×10^{-3}	1×10^{-3}	2×10^{-3}
Solids and Liquids using Estimated T_b ^b					
				^c	
2,6-Dichlorobenzonitrile	525	20(s)	6×10^{-4}	2×10^{-2}	4×10^{-4}
4,6-Dinitro-o-cresol	582	35(s)	4×10^{-4}	1×10^{-3}	4×10^{-5}
Trifluralin	635	30(l)	2×10^{-4}	6×10^{-5}	3×10^{-4}
Dinoseb	635	25(l)	5×10^{-5}	6×10^{-6}	5×10^{-5}
Carbofuran	570	33(s)	2×10^{-5}	3×10^{-4}	6×10^{-5}
Dicamba	570	25(s)	2×10^{-5}	2×10^{-4}	2×10^{-5}
Lindane	583	20(s)	9×10^{-6}	5×10^{-4}	8×10^{-6}
Aldrin	618	25(s)	6×10^{-6}	4×10^{-5}	8×10^{-7}
DDT	613	20(s)	2×10^{-7}	2×10^{-5}	2×10^{-7}
Endrin	618	20(s)	2×10^{-7}	7×10^{-5}	3×10^{-7}
Dieldrin	623	20(s)	1×10^{-7}	1×10^{-6}	1×10^{-7}

a. From Refs. 2, 5, 13, 14 and 16.

b. T_b estimated using methods of Chapter 12.

c. These values were obtained by using Method 1 to obtain an initial estimate for the supercooled liquid, and then applying the correction factor given in Eq. 14-10.

spill, for example, an order-of-magnitude estimate is usually sufficient. As shown in Tables 14-2 and 14-3, the maximum deviations for both methods are considerably less than this over the entire range of pressures.

TABLE 14-3

Average and Maximum Errors in Estimated Vapor Pressure^a

Pressure Range (mm)	Average Error (%)	Maximum Error (%)
Method 1		
10-760	2.7	+6.6
10 ⁻³ -10	86	+100
Method 2		
10-760	2.5	+7.1
10 ⁻³ -10	39	+50.0
10 ⁻⁷ -10 ⁻³	47	+200

a. Errors calculated for the chemicals listed in Table 14-2.
A larger number of significant figures than shown in
Table 14-2 for P_{vp} were used in the calculation of method
errors.

14-3 METHOD 1

Derivation. The first method uses the Antoine equation [1], which has the general form

$$\ln P_{vp} = A_2 - \frac{B_2}{T - C_2} \quad (14-11)$$

Applying Eqs. 14-5 and 14-6,

$$A_2 = \frac{B_2}{T_b - C_2} \quad (14-12)$$

and

$$B_2 = \frac{\Delta H_{vb}}{\Delta Z_b RT_b^2} [(T_b - C_2)^2] \quad (14-13)$$

Substituting Eqs. 14-12 and 14-13 in Eq. 14-11 yields

$$\ln P_{vp} = \frac{\Delta H_{vb} (T_b - C_2)^2}{\Delta Z_b R T_b^2} \left[\frac{1}{(T_b - C_2)} - \frac{1}{(T - C_2)} \right] \quad (14-14)$$

The parameter ΔZ_b is assumed to have the value of 0.97 [8], and T_b is generally known. What remains are techniques for evaluating ΔH_{vb} and C_2 . The constant C_2 is estimated via Thomson's rule [15], such that

$$C_2 = -18 + 0.19 T_b \quad (14-15)$$

The heat of vaporization at the boiling point, ΔH_{vb} , is evaluated using a simple method introduced by Fishtine [4], who modified the Kistiakovskii [6] equation to obtain

$$\frac{\Delta H_{vb}}{T_b} = \Delta S_{vb} = K_F (8.75 + R \ln T_b) \quad (14-16)$$

where K_F is derived from a consideration of the dipole moments of polar and nonpolar molecules. Table 14-4 lists values of K_F for various compound classes. Thus, the only input data needed is the normal boiling point, T_b . When T_b is not known, the estimation techniques outlined in Chapter 12 may be used.

For polar derivatives of benzene, Fishtine suggested that $K_F = 1 + 2\mu/100$, where μ is the dipole moment of the derivative. For naphthalene derivatives he suggests $K_F = 1 + \mu/100$. Methods of estimating dipole moments are given in Chapter 25. Special consideration must be given to hydrogen bonded systems; Table 14-5 lists values for aromatic phenols, diols, and amine compounds. These values are to be applied no matter what other polar group is present.

Method 1 is applicable only over the normal liquid range. Thus, it should only be used to estimate the vapor pressure of materials that are either in the liquid or vapor state at the temperature of interest. Method 2 (described later) is applicable for estimating the vapor pressures of liquids and solids.

Basic Steps

- (1) Obtain the normal boiling point T_b (K). If unavailable, use one of the estimation methods outlined in Chapter 12.
- (2) Obtain K_F from Table 14-4 or 14-5 as appropriate.
- (3) Calculate $\Delta H_{vb}/T_b$ using Eq. 14-16. The value of R is 1.987 cal/mol·K.

TABLE 14-4

 K_F Factors for Aliphatic and Alicyclic^a Organic Compounds

Compound Type	Number of carbon atoms (N) in compound, including carbon atoms of functional group											
	1	2	3	4	5	6	7	8	9	10	11	12-20
Hydrocarbons												
n-Alkanes	0.97	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Alkane isomers		1.01	1.01	1.01	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
Mono- and diolefins and isomers			1.00	1.00	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.00
Cyclic saturated hydrocarbons				1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Alkyl derivatives of cyclic saturated hydrocarbons				0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
Halides (saturated or unsaturated)												
Monochlorides	1.05	1.04	1.03	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.01
Monobromides	1.04	1.03	1.03	1.03	1.03	1.03	1.02	1.02	1.02	1.01	1.01	1.01
Moniodides	1.03	1.02	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.01
Polyhalides (not entirely halogenated)	1.05	1.05	1.05	1.04	1.04	1.04	1.03	1.03	1.03	1.02	1.02	1.01
Mixed halides (completely halogenated)	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Perfluorocarbons	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Compounds Containing the Keto Group												
Esters		1.14	1.09	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Ketones			1.08	1.07	1.06	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Aldehydes	-	1.09	1.08	1.08	1.07	1.06	1.05	1.04	1.04	1.03	1.02	1.01
Nitrogen Compounds												
Primary amines	1.16	1.13	1.12	1.11	1.10	1.10	1.09	1.09	1.08	1.07	1.06	1.05 ^b
Secondary amines		1.09	1.08	1.08	1.07	1.07	1.06	1.05	1.05	1.04	1.04	1.03 ^b
Tertiary amines			1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Nitriles	-	1.05	1.07	1.06	1.06	1.05	1.05	1.04	1.04	1.03	1.02	1.01
Nitro compounds	1.07	1.07	1.07	1.06	1.06	1.05	1.05	1.04	1.04	1.03	1.02	1.01

(Continued)

TABLE 14-4 (Continued)

Compound Type	Number of carbon atoms (N) in compound, including carbon atoms of functional group											
	1	2	3	4	5	6	7	8	9	10	11	12-20
Sulfur Compounds												
Mercaptans	1.05	1.03	1.02	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Sulfides		1.03	1.02	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Alcohols												
Alcohols (single-OH group)	1.22	1.31	1.31	1.31	1.31	1.30	1.29	1.28	1.27	1.26	1.24	1.24 ^b
Diols (glycols or condensed glycols)		1.33	1.33	1.33	1.33	1.33	1.33	1.33				
Triols (glycerol, etc.)			1.38	1.38	1.38							
Cyclohexanol, cyclohexyl methyl alcohol, etc.						1.20	1.20	1.21	1.24	1.26		
Miscellaneous Compounds												
Ethers (aliphatic only)		1.03	1.03	1.02	1.02	1.02	1.01	1.01	1.01	1.01	1.01	1.01
Oxides (cyclic ethers)		1.08	1.07	1.06	1.05	1.05	1.04	1.03	1.02	1.01	1.01	1.01

a. Carbocyclic or heterocyclic compounds having aliphatic properties.

b. For $N = 12$ only; no prediction is made for K_F where $N > 12$.

Notes:

1. Consider any phenyl group as a single carbon atom.
2. K_F factors are the same for all aliphatic isomers of a given compound. For example, $K_F = 1.31$ for *n*-butyl alcohol, *i*-butyl alcohol, *t*-butyl alcohol, and *s*-butyl alcohol.
3. In organometallic compounds, consider any metallic atom as a carbon atom.
4. For compounds not included in this table, assume $K_F = 1.06$.

Source: Fishline [4]

TABLE 14-5

Values of K_F for Aromatic Hydrogen Bonded Systems^a

Compound Type	K_F
Phenols (single -OH)	1.15
Phenols (more than one -OH)	1.23
Anilines (single -NH ₂)	1.09
Anilines (more than one -NH ₂)	1.14
N-substituted anilines (C ₆ H ₅ NHR)	1.06
Naphthols (single -OH)	1.09
Naphthylamines (single -NH ₂)	1.06
N-substituted naphthylamines	1.03

a. For mixed systems, K_F for the OH group takes precedence.
Thus, K_F for p-aminophenol is 1.15.

Source: Fishtine [4].

- (4) Assume $\Delta Z_b = 0.97$ [8].
- (5) Calculate C_2 using Eq. 14-15.
- (6) Insert the above values into Eq. 14-14 and calculate $\ln P_{vp}$.
- (7) Take the antilog and multiply by 760 to obtain the vapor pressure in mm Hg.

Example 14-1 Estimate the vapor pressure of benzene at 20°C, given
 $T_b = 353.1\text{K}$.

(1) From Table 14-4, $K_F = 1.00$

(2) From Eq. 14-16

$$\begin{aligned}\Delta H_{vb}/T_b &= 1.00 \times [8.75 + 1.987 \ln (353.1)] \\ &= 20.41 \text{ cal/mol}\cdot\text{K}\end{aligned}$$

(3) From Eq. 14-15

$$\begin{aligned}C_2 &= -18.00 + 0.19 (353.1) \\ &= 49.09\end{aligned}$$

(4) From Eq. 14-14

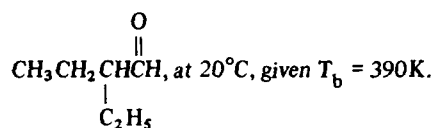
$$\ln P_{vp} = \frac{20.41 (353.1 - 49.09)^2}{0.97 \times 1.987 \times 353.1} \left[\frac{1}{(353.1 - 49.09)} - \frac{1}{(293 - 49.09)} \right]$$

$$= -2.24$$

$$P_{vp} = \text{antilog}(-2.24) \times 760 = 80.6 \text{ mm Hg}$$

The experimental value is 76 mm; hence, the deviation is 6.0%.

Example 14-2 Estimate the vapor pressure of 2-ethyl-butylaldehyde,



(1) From Table 14-4, $K_F = 1.06$

(2) From Eq. 14-16

$$\frac{\Delta H_{vb}}{T_b} = 1.06 [8.75 + 1.987 \ln (390)]$$

$$= 21.84$$

(3) From Eq. 14-15

$$C_2 = -18 + 0.19 (390)$$

$$= 56.1$$

(4) From Eq. 14-14

$$\ln P_{vp} = \frac{21.84 (390 - 56.1)^2}{0.97 \times 1.987 \times 390} \left[\frac{1}{(390 - 56.1)} - \frac{1}{(293 - 56.1)} \right]$$

$$= -3.972$$

$$P_{vp} = \text{antilog}(-3.972) \times 760 = 14.3 \text{ mm Hg}$$

The experimental value is 14 mm Hg, indicating a deviation of 2.3%.

14-4 METHOD 2

Derivation. As pointed out earlier, when Eq. 14-1 is integrated with the assumption that $\Delta H_v/\Delta Z$ is independent of temperature, the resulting expression yields inaccurate estimates of vapor pressure. However, if

the temperature dependence of ΔH_v can be accurately expressed, the resulting integrated form of Eq. 14-1 should be more accurate. One correlation that the author has found to be satisfactory is a modification of the Watson correlation [17]:

$$\Delta H_v = \Delta H_{vb} \left(\frac{1 - T/T_c}{1 - T_b/T_c} \right)^m \quad (14-17)$$

where m is a constant. Equation 14-17 contains the critical temperature T_c . The approximation $T_c \approx 3 T_b/2$ may be used, yielding

$$\Delta H_v \approx \Delta H_{vb} (3 - 2T_{\rho b})^m \quad (14-18)$$

where $T_{\rho b} = T/T_b$. For most organic materials the ratio T_c/T_b varies from 1.3 to 1.7; however, at temperatures below the boiling point, the maximum deviations in ΔH_v using Eq. 14-18 instead of Eq. 14-19 are + 2% and -5% respectively. When Eq. 14-18 is substituted into Eq. 14-1 and the result is integrated twice, by parts, the result is

$$\begin{aligned} \ln P_{vp} \approx & - \frac{\Delta H_{vb}}{\Delta Z_b R T_b} \left[\left(\frac{(3 - 2T_{\rho b})^m}{T_{\rho b}} + 2m (3 - 2T_{\rho b})^{m-1} \ln T_{\rho b} \right) \right]_1^{T_{\rho b}} \\ & - 4m(m-1) \int_1^{T_{\rho b}} (3 - 2T_{\rho b})^{m-2} \ln T_{\rho b} dT_{\rho b} \end{aligned} \quad (14-19)$$

The integration may be carried out to as many terms as desired; however, sufficient accuracy is obtained by setting the integral in Eq. 14-19 equal to zero. The final result is

$$\ln P_{vp} \approx \frac{\Delta H_{vb}}{\Delta Z_b R T_b} \left[1 - \frac{(3 - 2T_{\rho b})^m}{T_{\rho b}} - 2m (3 - 2T_{\rho b})^{m-1} \ln T_{\rho b} \right] \quad (14-20)$$

The value of m in Eq. 14-20 depends upon the physical state at the temperature of interest. For all liquids, $m = 0.19$. For solids the following values are recommended:

$$T_{\rho b} > 0.6; m = 0.36$$

$$0.6 > T_{\rho b} > 0.5; m = 0.8$$

$$T_{\rho b} < 0.5; m = 1.19$$

Basic Steps

- (1) Obtain T_b (K) from the literature. If it is unavailable, use one of the estimation methods outlined in Chapter 12. (Note that T_{ρ_b} in Eq. 14-20 is equal to T/T_b .)
- (2) Obtain K_F from Table 14-4 or 14-5 as appropriate.
- (3) Set $m = 0.19$ for liquids. For solids: if $T_{\rho_b} > 0.6$, $m = 0.36$; if $0.6 > T_{\rho_b} > 0.5$, $m = 0.8$; and if $T_{\rho_b} < 0.5$, $m = 1.19$.
- (4) Calculate $\Delta H_{vb}/T_b$ from Eq. 14-16. The value of R is 1.987 cal/mol·K.
- (5) Assume $\Delta Z_b = 0.97$.
- (6) Insert values obtained above into Eq. 14-20 and calculate $\ln P_{vp}$.
- (7) Take the antilog and multiply by 760 to obtain the vapor pressure in mm Hg.

Example 14-3 Estimate the vapor pressure of benzene at 20°C, given $T_b = 353.1\text{K}$.

- (1) From Table 14-4, $K_F = 1.00$.
- (2) Since benzene is a liquid at 20°C, $m = 0.19$.
- (3) $T_{\rho_b} = 293/353.1 = 0.830$
- (4) From Eq. 14-16

$$\begin{aligned}\frac{\Delta H_{vb}}{T_b} &= 1.00 \times [8.75 + 1.987 \ln (353.1)] \\ &= 20.4 \text{ cal/mol}\cdot\text{K}\end{aligned}$$

- (5) From Eq. 14-20

$$\begin{aligned}\ln P_{vp} &= \frac{20.4}{0.97 \times 1.987} \left\{ 1 - \frac{[3 - 2(0.830)]^{0.19}}{0.830} - \right. \\ &\quad \left. -2(0.19) [3 - 2(0.830)]^{-0.81} \ln (0.830) \right\} \\ &= -2.3\end{aligned}$$

$$P = \text{antilog}(-2.3) \times 760 = 76 \text{ mm Hg}$$

Since the experimental value is 76 mm, the deviation is 0%.

Example 14-4 Estimate the vapor pressure of DDT at 20°C.

- (1) As DDT does not have a normal boiling point, the techniques of Chapter 12 are used to estimate it. T_b (est.) = 613K via Meissner's method (§ 12-3).
- (2) From the listing for polyhalides in Table 14-4 (see also note 1), $K_F = 1.05$.
- (3) $T_{pb} = 293/613 = 0.478$
- (4) As DDT is a solid at 20°C and $T_{pb} < 0.5$, $m = 1.19$.
- (5) From Eq. 14-16

$$\begin{aligned}\frac{\Delta H_{vb}}{T_b} &= 1.05 \times [8.75 + 1.987 \ln (613)] \\ &= 22.6 \text{ cal/mol}\cdot\text{K}\end{aligned}$$

- (6) From Eq. 14-20

$$\begin{aligned}\ln P_{vp} &= \frac{22.6}{0.97 \times 1.987} \left\{ 1 - \frac{[3 - 2(0.478)]^{1.19}}{0.478} \right. \\ &\quad \left. - 2(1.19) [3 - 2(0.478)]^{0.19} \ln (0.478) \right\} \\ &= -22.1\end{aligned}$$

$P = \text{antilog}(-22.1) \times 760 = 1.9 \times 10^{-7} \text{ mm Hg}$, which agrees with the experimental value of 2×10^{-7} .

14-5 ESTIMATION FROM BOILING POINTS AT REDUCED PRESSURE

Quite often, data are available in which a boiling point at reduced pressure is given. As pointed out in §14-2, an estimate of the ratio $\Delta H_v/T$ must then be made. A simple but adequate approximation may be obtained by considering the origin of the Kistiakovskii equation (Eq. 14-16). At the normal boiling point, Eq. 14-16 may be written as

$$\Delta H_{vb} = K_F P_{vp} V_{vb} \ln V_{vb} \quad (14-21)$$

where P_{vp} = pressure in atmospheres (= 1 atm at T_b)

V_{vb} = molar volume of the vapor at T_b (cm^3).

If we use the ideal gas law, Eq. 14-16 is obtained.

It seems reasonable that an approximate value of $\Delta H_{v1}/T_1$ can be obtained at other temperatures by writing

$$\Delta H_{v1} = K_F P_1 V_{v1} \ln V_{v1} \quad (14-22)$$

Again, using the ideal gas law, we obtain

$$\frac{\Delta H_{v1}}{T_1} \approx K_F R \ln \left(\frac{RT_1}{P_1} \right) \quad (14-23)$$

where R , outside the parentheses, has the value 1.987 cal/mol·K and a value of 82.05 cm³·atm/K, inside the parentheses. Equation 14-23 can be rearranged to yield

$$\frac{\Delta H_{v1}}{T_1} \approx K_F [8.75 + R (\ln T_1 - \ln P_1)] \quad (14-24)$$

With this modification, the reference temperature T_1 can be substituted directly for T_b in Eq. 14-14 (Method 1) to yield

$$\ln P_{vp} = \ln P_1 + \frac{\Delta H_{v1} (T_1 - C_2)^2}{\Delta Z_b R T_1^2} \left[\frac{1}{(T_1 - C_2)} - \frac{1}{(T - C_2)} \right] \quad (14-25)$$

The same substitution is not strictly valid for Eq. 14-20 (Method 2). However, for practical purposes, little error is introduced if this is done. Thus

$$\ln P_{vp} = \ln P_1 + \frac{\Delta H_{v1}}{\Delta Z_b R T_1} \left\{ 1 - [3 - 2(T/T_1)]^m \frac{T_1}{T} - 2m [3 - 2(T/T_1)]^{m-1} \ln (T/T_1) \right\} \quad (14-26)$$

Equation 14-25 is valid for liquids while Eq. 14-26 is applicable to liquids and solids.

Basic Steps. The basic steps are similar to those outlined in §14-3 (Method 1) or §14-4 (Method 2). The only differences are: (1) T_1 is substituted for T_b , and (2) Eqs. 14-24 and 14-25 or 14-26 are used to

estimate ΔH_{v1} and P_{vp} , respectively. P_1 in Eqs. 14-24, -25 and -26 must be expressed in atmospheres.

Example 14-5 Estimate the vapor pressure of acetone cyanohydrin, $\text{CH}_3\text{C}(\text{OH})(\text{CN})\text{CH}_3$, at 20°C , given that $P_1 = 23$ mm and $T_1 = 354\text{K}$.

(1) As the material is a liquid at 20°C , Eq. 14-25 may be used.

(2) From Table 14-4, Note 4, $K_F = 1.06$.

$$(3) \quad P_1 = \frac{23}{760} = 3.03 \times 10^{-2} \text{ atm.}$$

(4) From Eq. 14-24

$$\begin{aligned} \frac{\Delta H_{v1}}{T_1} &= 1.06 \left\{ 8.75 + 1.987 [\ln(354) - \ln(0.0303)] \right\} \\ &= 29.0 \text{ cal/mol}\cdot\text{K} \end{aligned}$$

(5) From Eq. 14-15

$$\begin{aligned} C_2 &= -18 + 0.19 (354) \\ &= 49.3 \end{aligned}$$

(6) From Eq. 14-25

$$\begin{aligned} \ln P_{vp} &= \ln(0.0303) + \frac{29.0 (354 - 49.3)^2}{0.97 \times 1.987 \times 354} \left[\frac{1}{(354 - 49.3)} - \frac{1}{(293 - 49.3)} \right] \\ &= -6.74 \end{aligned}$$

$$P_{vp} = \text{antilog}(-6.74) \times 760 = 0.9 \text{ mm}$$

The experimental value is 0.8 mm, indicating a deviation of + 12.5%.

Example 14-6 Estimate the vapor pressure, at 298K, of methylene diphenyl isocyanate, $[(\text{OCN})\text{C}_6\text{H}_4]_2\text{CH}_2$, given that $P_1 = 5$ mm and $T_1 = 463\text{K}$.

(1) As the compound is a solid (m.p. = 41°C) at 298K (25°C), Eq. 14-26 will be used.

(2) From Table 14-4, Note 4, $K_F = 1.06$

$$(3) \quad P_1 = \frac{5}{760} = 6.58 \times 10^{-3} \text{ atm}$$

$$T/T_1 = 298/463 = 0.644$$

(4) From Eq. 14-24

$$\frac{\Delta H_{v1}}{T_1} = 1.06 \left\{ 8.75 + 1.987 [\ln(463) - \ln(0.0066)] \right\}$$

$$= 32.8 \text{ cal/mol}\cdot\text{K}$$

- (5) As we do not know the normal boiling point, a value of 0.8 is chosen for m .
(If more confidence in the selected value of m is desired, a boiling point could be estimated via the methods in Chapter 12.)

- (6) From Eq. 14-26

$$\ln P_{vp} = \ln(0.0066) + \frac{32.8}{0.97 \times 1.987} \left\{ 1 - \frac{[3 - 2(0.644)]^{0.8}}{0.644} - 2 \times 0.8 \times [3 - 2(0.644)]^{-0.2} \times \ln(0.644) \right\}$$

$$= -17.9$$

$$P_{vp} = \text{antilog}(-17.9) \times 760 = 1.29 \times 10^{-5} \text{ mm}$$

The experimental value is 1.0×10^{-5} mm, indicating a deviation of 29%.

14-6 AVAILABLE DATA

Vapor pressure data for petroleum chemicals can be obtained from the general compilations listed in Appendix A. References 2, 5, and 14 list the vapor pressures of some other materials, such as pesticides.

14-7 SYMBOLS USED

A_1	= constant in Eq. 4-3
A_2	= constant in Eq. 14-12
B_1	= constant in Eq. 14-3
B_2	= constant in Eq. 14-12
C_2	= constant in Eq. 14-12
ΔH_v	= heat of vaporization (cal/mol)
ΔH_{v1}	= heat of vaporization at T_1 (cal/mol)
ΔH_{vb}	= heat of vaporization at the normal boiling point (cal/mol) in Eq. 14-16
K_F	= constant in Eq. 14-16
K_{ow}	= octanol-water partition coefficient
m	= exponent in Watson correlation (Eq. 14-17)
P_1	= reference vapor pressure (mm Hg)
P_c	= critical pressure (atm)
P_{vp}	= vapor pressure (mm Hg)
R	= gas constant $\equiv 1.987 \text{ cal/mol}\cdot\text{K}$ ($= 82.057 \text{ cm}^3\cdot\text{atm/mol}\cdot\text{K}$ in Eq. 14-2)

- ΔS_{vb} = entropy of vaporization at the normal boiling point
(cal/mol·K) in Eq. 14-16
 t = temperature (°C)
 T = temperature (K)
 T_1 = reference temperature (K)
 T_b = temperature of the normal boiling point (K)
 T_c = critical temperature (K)
 T_m = melting point (K)
 T_{ρ_b} = T/T_b
 V_{vb} = molar volume of vapor at T_b (cm³)
 V_{v1} = molar volume of vapor at T_1 (cm³)
 ΔV = volume difference (cm³/mol)
between vapor and liquid in Eq. 14-2
 ΔZ = compressibility factor in Eq. 14-2
 ΔZ_b = compressibility factor at the normal boiling point

Subscripts

- b = boiling point
 c = critical point
 m = melting point
 ρ = ratio
 v = vapor, vaporization
 vp = vapor; used with P (P_{vp}) to denote vapor pressure

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15

VOLATILIZATION FROM WATER

Richard G. Thomas

15-1 INTRODUCTION

The vaporization of organic chemicals from water bodies is an important mass-transfer pathway from water to air. Knowledge of volatilization rates is necessary to determine the amount of chemical that enters the atmosphere and the change of pollutant concentrations in water bodies. The transfer process from the water to the atmosphere is dependent on the chemical and physical properties of the pollutant in question, the presence of other pollutants, and the physical properties (e.g., flow velocity, depth, and turbulence) of the water body and atmosphere above it. The factors that control volatilization are the solubility, molecular weight, and vapor pressure of the chemical and the nature of the air-water interface through which it must pass.

The mathematical modeling of volatilization involves the use of interphase exchange coefficients that depend on the properties mentioned above, some of which are difficult to measure or estimate in the actual environment. They can be measured under controlled laboratory conditions, but the results often cannot be extended with confidence to the varied and changeable conditions encountered in the environment. Part of this difficulty is due to the lack of environmental volatilization data against which laboratory-based hypotheses can be tested.

Thus, estimates of volatilization rates from surface waters on the basis of mathematical data and laboratory measurements are necessarily

of unknown precision. No attempt is made here to give a quantitative estimate of the error implicit in the methods to be described; however, comparisons of experimental results with theoretical predictions indicate that these predictive techniques are generally in agreement with actual processes within about a factor of ten at the most and probably within a factor of two or three in most cases.

Volatilization rates from water vary over a large range. Some chemicals volatilize from well-mixed surface waters quite rapidly, with a half-life on the order of hours; others may remain in the water almost indefinitely unless they degrade or are removed by a different transfer mechanism. For example, trichloroethylene has a computed half-life of three to five hours for volatilization from a river; the pesticide dieldrin, on the other hand, volatilizes more slowly than water and its concentration would actually increase, at least in the short term, so that its half-life due to volatilization is on the order of a year or more.

This chapter describes the volatilization process, discusses some of the theoretical methods that have been developed to model the volatilization of chemicals from surface waters, and presents a method for estimating the rate at which this process takes place. Various organic chemicals are listed together with their properties related to volatilization, and basic steps and examples are presented to show how to compute the mass transfer coefficients and half-lives in water for organic chemicals.

15-2 MODELING VOLATILIZATION IN THE ENVIRONMENT

Many factors affect the volatilization process. Although these factors are known, they can change rapidly and over a wide range in a natural environment. This complicates the task of providing average or mean values for use in an analytical model. The processes are often nonlinearly interdependent and do not behave in simple, deterministic ways.

Specifically, the volatilization process depends on the thermodynamic or physical properties of a chemical, particularly its aqueous solubility, vapor pressure, Henry's law constant and diffusivity coefficient, and the presence of modifying materials such as adsorbents, organic films, electrolytes, and emulsions [10,11]. The true "dissolved" and "total" concentrations are highly dependent on the presence of these modifying materials [3]. The values of the rate-controlling factors also depend on the physical and chemical properties of the water body, such as its depth, flow rate, the presence of waves, sediment content, and the

other pollutants present. Atmospheric conditions, particularly wind speed and stability, also affect the rate-controlling factors. Volatilization is, in general, relatively temperature-insensitive, since the principal effect of temperature is on the vapor pressure. The latter has little influence on volatility except for the few classes of chemicals whose volatilization is controlled by processes that occur in the vapor phase. (These are addressed later.)

The transport and transfer of a chemical may involve several sequential stages depending on the type of water body involved. Each of these stages has a characteristic rate, diffusion velocity, or resistance [12], and the slowest stage controls the overall volatilization rate. For a stratified lake, the stages may be: (1) release from the sorbed state on sediments; (2) diffusion through the hypolimnion; (3) diffusion through the thermocline; (4) diffusion through the epilimnion to the near surface (approximately one millimeter below the surface); (5) diffusion through the liquid surface "stagnant film"; (6) transfer across the water/air interface; and (7) diffusion through the atmospheric film to the bulk of the atmosphere. Transfer through the different layers in the water can occur only by bulk movement (as in the case of turbulent eddy motion) or by molecular diffusion [9,14]. If the water body is well mixed, as in a flowing river, most of the resistance to transport lies in the gas- and liquid-phase interfacial layers a few millimeters or centimeters above or below the surface [10,11,13]. The interface between the gas- and liquid-phase interfacial layers is believed to offer little or no resistance. Hence, a concentration gradient develops in the surface layers. For most substances and most water bodies, resistance in one phase tends to dominate [9].

Under given conditions of turbulence, layer thicknesses vary both spatially and temporally [9]. High turbulence in the liquid causes the liquid film or boundary layer to be thin; similarly, high turbulence in the gas causes the gas layer to be thin [18]. Wind also modifies surface hydrodynamics, affecting chemical mass-transfer coefficients.

Vertical transport to the surface of rivers and large lakes is controlled by currents, both direct and wind-induced. In rivers, diffusion from the bottom to the surface is accelerated by eddies caused by the interaction of the current with the bottom [12]. Since turbulence is generated mainly at the river bottom, the deeper rivers have more quiescent surfaces, and the transfer resistance tends to be higher [10]. In lakes, wind speed and fetch (the length of water over which the wind blows) are the controlling factors: turbulence is normally present in the atmosphere, but there is usually little in the water unless it is induced by wind-generated waves on the surface, subsurface springs, or thermally driven convective

action. Regardless of the cause, turbulence can greatly increase the liquid-phase exchange coefficient.

Horizontal and vertical turbulent diffusion affect the rate and extent of mixing [10]. In water, horizontal turbulent diffusion is usually an order of magnitude faster than vertical turbulent diffusion; as a result, pollutants spread faster laterally than they do vertically. In the atmosphere, vertical diffusion is usually more rapid than in the water, and chemicals are transported from the interface quickly. During the stable conditions of temperature inversions (when temperature increases with height), however, vertical atmospheric diffusion decreases, the water surface is calmer, resistance to chemical transfer through the air and water boundary films increases, and volatilization rates decrease.

Sediments are important because they can act as permanent or temporary sinks for chemicals in the water [10,12]. The exchange between the water column and the sediment has a significant effect on the rate of removal from the water proper. The sediment/water partition (sorption) coefficient is affected by the characteristics of the sediment, e.g., type, spatial distribution, particle size and density, and organic matter. Chapter 4 of this handbook describes the adsorption phenomenon and methods for estimating adsorption coefficients.

15-3 APPROACHES TO ESTIMATION OF THE VOLATILIZATION RATE

The two-layer film or resistance concept of the interface — i.e., the theory that resistance to mass transport exists in both the gas- and liquid-phase interfacial layers — was first discussed in 1923 [23]. However, most of the analytical work has been done only in the last several years. Four basic approaches have been used; these are described below.

Method of Mackay and Wolkoff. These authors [14] analyzed the volatilization of chemicals from bodies of water on the basis of thermodynamic equilibrium considerations. This theory expresses the flux from a solution in water to the air above in terms of the ratio of contaminant mass in the vapor phase to the total vapor mass of the water plus chemical, expressed as a function of the chemical vapor pressure. The following assumptions are made:

- (1) The contaminant concentration used is that which is truly in solution; there are no colloidal, suspended, ionic, complexed, or adsorbed forms of the contaminant.

- (2) The concentration of the diffusing substance in the vapor adjacent to the interface is that which is in equilibrium with the concentration in the liquid at the interface.
- (3) Diffusion or mixing in the liquid is sufficiently rapid that concentrations at the liquid side of the interface are equal to concentrations in the bulk of the liquid (which implies thorough mixing).
- (4) The water evaporation rate is negligibly affected by the presence of the contaminant.

Ancillary to these assumptions are two others that affect the utility of the theory: (a) evaporation is the limiting process in the total volatilization process, and (b) there are no concentration gradients in the upper layers due to the evaporation. The latter follows from assumption (3) above, namely, that there is perfect mixing in the water phase and equilibration between the water and air. Because of these assumptions, this method will overestimate the volatilization rate if mixing or diffusion in the water body is slow, thus retarding the overall process.

This method is applicable only to a restricted class of compounds and is thus not recommended for general use. The significant conclusion reached by Mackay and Wolkoff was that volatilization may be significant, i.e., half-lives short, for compounds which have vapor pressures much lower than that of water, provided that the compound is sparingly soluble.

In a subsequent study, Mackay and Leinonen [11] extended the method to include consideration of the resistance due to diffusion in the liquid phase and estimated volatilization half-lives for all classes of compounds. Their work was an extension of methods previously developed by Liss and Slater [9].

Method of Liss and Slater. The volatilization process was analyzed on the basis of a two-layer film by Liss and Slater [9]. This has been shown [16] to be a more realistic approach than that originally developed by Mackay and Wolkoff [14]. The main water body is assumed to be well mixed, with a thin layer on the surface in which there is a concentration gradient. The air above is assumed to be well mixed (i.e., the background concentration is low), and a thin layer in contact with the surface contains another concentration gradient. (Thus, diffusion in the water body is not assumed to be a rate-limiting process.) At the interface between these two layers is a concentration discontinuity, and the ratio of con-

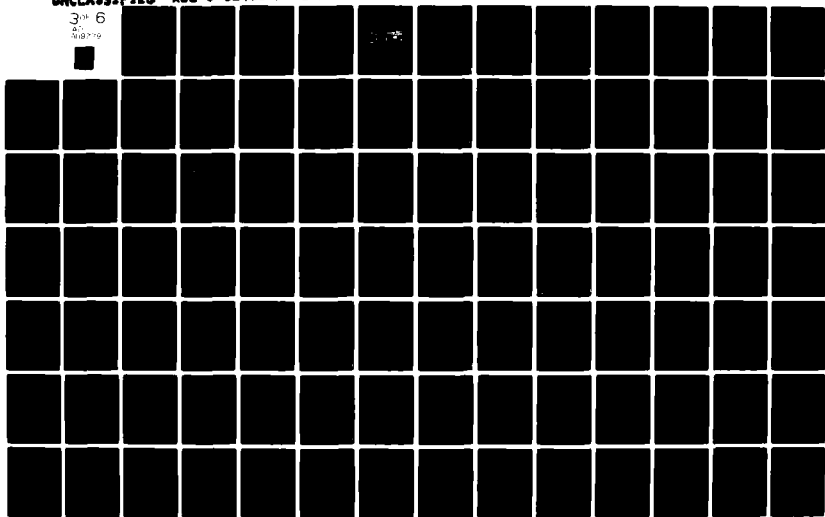
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centrations across it (air to water) is assumed to equal the Henry's law constant.

Transfer through these films is by straightforward molecular diffusion. The molecules are assumed to diffuse through the layers at a rate dependent on the phase exchange coefficients found in the equations rather than to vaporize directly from solution along with the water vapor.

Environmental conditions leading to turbulence in either phase influence the thickness, diffusivity, resistance, and geometry of the layers. Since resistance to diffusion is dependent on layer geometry and composition, the molecular phase exchange coefficients used in the determination of the overall mass transfer are affected by environmental conditions. These coefficients are somewhat empirical, in that they cannot yet be readily computed using basic physical principles, but values for the gas-phase and liquid-phase exchange constants have been determined for the transfer of certain gases across the air/sea interface. These can be adjusted to apply to certain other classes of chemicals; however, the best method for doing this is not clear [10,15]. Schwarzenbach *et al.* [17] indicate that the coefficients based on open-ocean data may overestimate the transfer in lakes.

Method of Chiou and Freed. Chiou and Freed [1,2] present another method for estimating the volatilization of chemicals. It appears to be based on gas dynamic and thermodynamic considerations involving the mean free path of molecules and the vapor pressures of the chemical. A Langmuir-type equation is used to describe observed rates of volatilization from both single-component and multicomponent systems. No data have been offered to support the validity of this method, and its efficacy is not known. Little notice has been taken of it in recent studies of volatilization of chemicals from water.

Method of Smith *et al.* This approach is based on reaeration studies by Tsivoglou [21], who demonstrated that inert gases could be used as tracers for oxygen reaeration measurement. Since the transfer rates of oxygen and the inert gases are controlled by diffusion in the near surface film, these rates are similar; a correction is necessary only for the differing diffusivities, which are related primarily to molecular diameter. Smith *et al.* [18,19] applied this approach to other compounds and verified that the magnitude of the diffusivity correction term was as expected for compounds that experience the same liquid-phase resistance as oxygen. Compounds with lower Henry's law constants which also experience a gas-phase resistance volatilize more slowly, so this method of approximation is not applicable to such compounds.

For the class of compounds to which it is applicable, the advantage of this approach is that the volatilization rate can be related to the rate of oxygen reaeration. The latter is known for natural systems such as rivers and lakes. If one can obtain a laboratory-measured ratio of the reaeration rate of a chemical to that of oxygen, it can simply be multiplied by the environmental value of oxygen reaeration to yield an environmental value of the volatilization rate constant for the chemical. These investigators have also developed procedures for deriving the ratio when an experimental value cannot be found.

Smith *et al.* have demonstrated that their method is valid for the class of chemicals which have high volatility, high molecular weight, and low solubility (i.e., high Henry's law constants).

15-4 METHOD ERRORS

The environmental, physical, and chemical processes that control the volatilization rate have been described above. Their number and variety indicate the difficulties involved in devising an adequate model of the process. The fundamental mechanisms are reasonably well understood, however, and can be described by relatively simple mathematical expressions [10]; the results are often practically the same as those from more sophisticated models. The present inadequacies are primarily due to a lack of data for some of the parameters in the equations [10].

At the most basic level, some properties of chemicals may not be accurately known; these are needed to determine the Henry's law constant, which indicates the propensity of a chemical to volatilize. The gas- and liquid-phase exchange coefficients, on which the predictive techniques ultimately depend, are not known with certainty for diverse environmental conditions and a wide range of chemicals. Environmental and hydrodynamic factors that affect the movement of a chemical in water and its transfer into the air are difficult to quantify and relate to the volatilization rate; these factors may include wind speed, stratification, sediment content, and the presence of other pollutants. The range of values for these factors over a period of time, their variable nature, and their nonlinear interdependencies indicate the problems inherent in using time-averaged or mean values and reduce the validity of the calculations.

The overall environmental mass transfer coefficient for a particular chemical leaving a given water body, which is dependent on gas- and liquid-phase transfer coefficients and chemical properties, is difficult to

predict on the basis of laboratory studies. This is especially true if average values are desired, since the phase exchange coefficients are sensitive to variable environmental and hydrodynamic factors [17]. The methods used for estimating the exchange coefficients have been verified for only a few chemicals in a few laboratory experiments using stirrers and fans to simulate environmental conditions [3-5,8,14,16,18,19]. The overall volatilization rates measured in these experiments are often quite similar to those computed by theoretical methods [20]. This agreement may be fortuitous, however, since the basic factors are so dissimilar: the computations use phase exchange coefficients based loosely on environmental data, while the experiments use measured rates of stirring, air speed, etc. Nevertheless, the differences between experiment and computation are well within an order of magnitude, lending credibility to the predictive techniques.

Schwarzenbach *et al.* [17], in a study of dichlorobenzene (DCB) and tetrachloroethylene in Lake Zurich, Switzerland, suggested that the average mass transfer coefficient computed from an overall mass balance is about a factor of ten larger than that derived from mass balance computations based on other measurements of DCB in the lake. However, they note that their observed value of the overall mass transfer coefficient for the lake compares well with those found in a similar study of small Canadian lakes by different investigators.

The laboratory-based volatilization rates (computed) are comparable to those found for the open ocean; this is not surprising, as the phase exchange coefficients used in the calculations are based on open-ocean data. It may be incorrect to apply open-ocean data to lakes and other smaller bodies of water, but this question has not been discussed in the literature.

In view of these observations and the difficulty of performing in-situ volatilization experiments, it is not possible to quantify the error in the calculated values of the volatilization rate constants. The lake example indicates that the error may be as large as a factor of ten, although laboratory data suggest that it could be much less. When one is applying the results of calculations to actual environmental situations, it would probably be advisable to assume that the values of volatilization rate may be high by a factor of ten at most and low by a smaller factor of possibly three.

15-5 METHODS OF ESTIMATION

Recommended General Method. The methods of estimation recommended in this chapter follow the two-film concept for estimating the flux of volatiles across the air-water interface. This was described by Liss and Slater [9] and extended by Mackay and others [3,10-15]. Additional refinements suggested by other investigators are introduced where useful. Figure 15-1 shows the basics of this concept.

The method is based on a finite difference approximation to Fick's law of diffusion, which can be written as

$$N = k \Delta C \quad (15-1)$$

where

- N = flux ($\text{g}/\text{cm}^2 \cdot \text{s}$)
- k = D/z , a first-order exchange constant (cm/s)
- D = coefficient of molecular diffusion of chemical in the film (cm^2/s)
- z = film thickness (cm)
- ΔC = concentration difference across the film (g/cm^3)

In a steady-state process, Eq. 15-1 becomes

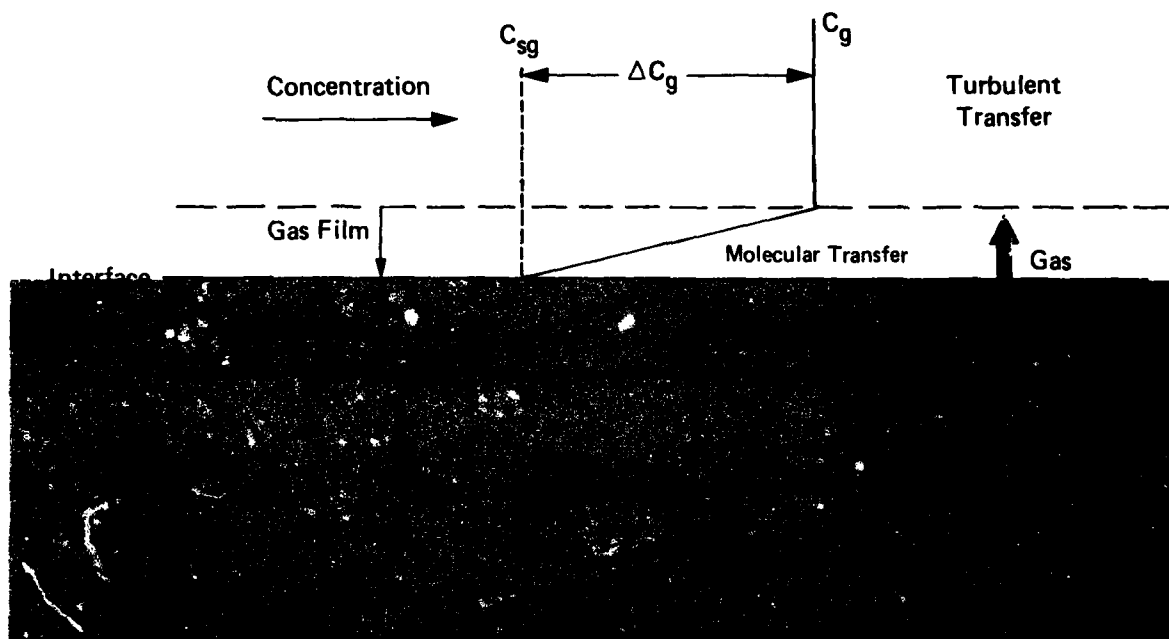
$$N = k_g (C_g - C_{sg}) = k_l (C_{sl} - C_l) \quad (15-2)$$

where

- k_g = gas-phase exchange coefficient (cm/s)
- C_g = concentration in gas phase at the outer edge of the film (g/cm^3)
- C_{sg} = concentration in gas phase at interface (g/cm^3)
- k_l = liquid-phase exchange coefficient (cm/s)
- C_{sl} = concentration in liquid phase at interface (g/cm^3)
- C_l = concentration in liquid phase at the outer edge of the film (g/cm^3)

The nondimensional Henry's law constant (H') relates the concentration of a compound in the gas phase to its concentration in the liquid phase:

$$H' = C_{sg}/C_{sl} \quad (15-3)$$



Source: Liss and Slater [9].

FIGURE 15-1 Two-Layer Model of Gas-Liquid Interface

Equation 15-2 can then be written as

$$N = \frac{C_g - H'C_l}{1/k_g + H'/k_l} = \frac{C_g/H' - C_l}{1/k_l + 1/H'k_g} \quad (15-4)$$

The overall mass transfer coefficients for the gas phase (K_G) and liquid phase (K_L) can be defined as follows:

$$1/K_G = 1/k_g + H'/k_l \quad (15-5)$$

and

$$1/K_L = 1/k_l + 1/H'k_g \quad (15-6)$$

By substitution in Eq. 15-4,

$$N = K_G (C_g - H'C_l) = K_L (C_g/H' - C_l) \quad (15-7)$$

The Henry's law constant can also be written in the form:

$$H = P_{vp}/S \quad (15-8)$$

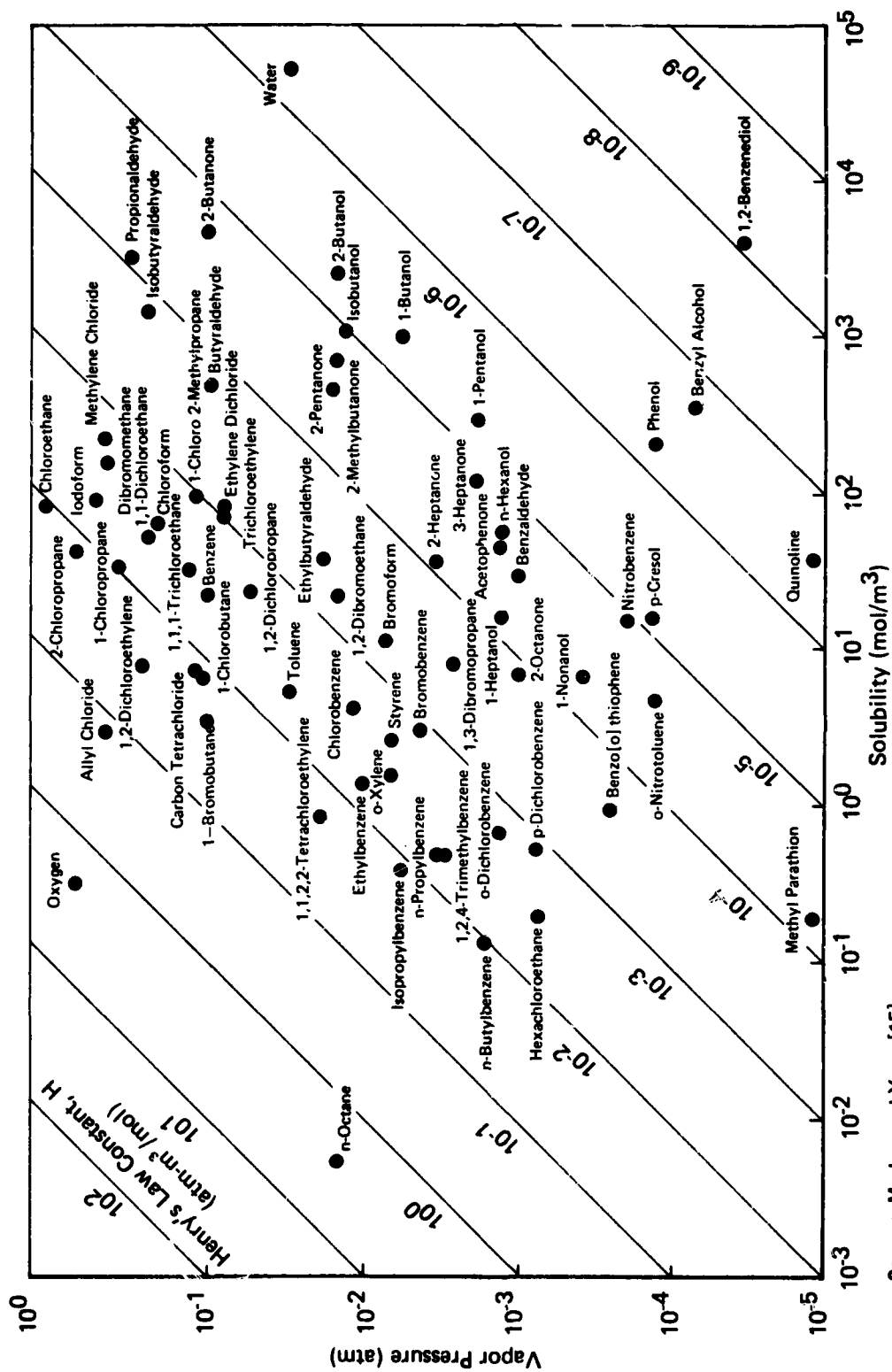
where P_{vp} is in atm, S is in mol/m³, and H is in atm-m³/mol. Figure 15-2, a graphical representation of Eq. 15-8, shows values of H for water, air, and numerous organic compounds.

When H is calculated by Eq. 15-8, the data must be for the same temperature and applicable to the same physical state of the compound. For example, P_{vp} for a liquid should not be divided by S for the solid state. (This error can occur if P_{vp} is estimated by extrapolating data from higher pressures.) Furthermore, only data for the pure compound should be used, as the vapor pressures and solubilities of mixtures — e.g., polychlorinated biphenyl isomers — may be suspect.

Note that Eq. 15-8 is only approximate. If measured values of P_{vp} and S are not available, they can be estimated by methods given in Chapters 14 and 2, respectively. An alternate method of estimating S , via estimated activity coefficients, is provided in Chapters 3 and 11.

Mackay and Leinonen [11] give a slightly different but equivalent expression for $1/K_L$ to be used when H is computed according to Eq. 15-8:

$$1/K_L = 1/k_l + 1/(Hk_g/RT) \quad (15-9)$$



Sources: Mackay and Yuen [15].

FIGURE 15-2 Solubility, Vapor Pressure and Henry's Law Constant for Selected Chemicals

where T is the absolute temperature (K) and R is the gas constant, 8.2×10^{-5} atm-m³/mol-K. (At 20°C, $RT = 2.4 \times 10^{-3}$ atm-m³/mol.) Equations 15-6 and 15-9 give identical values of $1/K_L$, since H/RT equals H' .

The same authors give the following equation for the flux:

$$N = K_L \left(C - \frac{P}{H} \right) \quad (15-10)$$

P/H must be expressed in g/cm³. If we assume the background atmospheric level to be negligible and integrate Eq. 15-10, the concentration at any time t can be expressed as

$$C = C_0 e^{-k_v t} = C_0 e^{-K_L t/Z} \quad (15-11)$$

where

- C_0 = initial concentration (g/cm³)
- k_v = K_L/Z = volatilization rate constant
- Z = mean depth of the water body (cm)

The half-life can be written as

$$\tau_{1/2} = 0.69 Z/K_L = 0.69/k_v \quad (15-12)$$

The term $1/K_L$ ($=R_L$) can be thought of as the total resistance to flux [2]. It depends on the exchange constants of the individual phases and the value of the Henry's law constant. Similarly, the individual terms $1/k_l$ and RT/Hk_g (or $1/H'k_g$) can be thought of as liquid-phase resistance r_l and gas-phase resistance r_g respectively. The values of these resistances indicate the relative importance of the gas and liquid phases in the exchange of a compound.

In addition to the resistances offered by the gas and liquid phases, another resistance can be analyzed [15] — namely, the resistance r_w to transfer from the bulk of the water body to the interface. (This resistance can be added to r_l and r_g to give the total resistance, R_L .) The bulk water resistance can be expressed as

$$r_w = \tau_D/Z \quad (15-13)$$

where τ_D is a characteristic time for the eddying motion of a turbulent water body to transport the volatile material to the surface. The value of τ_D indicates whether volatilization is limited by turbulent diffusion to the surface.

Associated with this transport is a turbulent diffusivity coefficient, which is a measure of the efficiency of macroscopic eddy motion in mixing the water. Because of stream geometry, the turbulent diffusivity takes on different values associated with different directions. Generally the value in the longitudinal direction, which is usually reported in the literature, is much larger than the values for the other directions because of larger eddy scale and intensity. Elder [6] relates the perpendicular turbulent diffusivity, D_z , to the longitudinal value, D_L , by

$$D_z \approx 0.039 D_L \quad (15-14)$$

The time τ_D associated with movement a mean distance Z , which in this case is the mean depth of the water body, is

$$\tau_D = Z^2 / 1.3 D_z \quad (15-15)$$

If this time is assumed to be equivalent to the half-life for the turbulent transfer process from depth Z to the surface, it can be compared with the volatilization half-life given in Eq. 15-12.

Typical values of the aquatic turbulent diffusivity are shown in Table 15-1. Values for streams, rivers, and estuaries were given as longitudinal diffusivities and converted to perpendicular values by Eq. 15-14.

TABLE 15-1

Typical Values of Aquatic Turbulent Diffusivities

Water Body	D_z (m^2/sec)	Source
Flumes and Small Streams	10^{-4} to 10^{-2}	} Gloyne [7]
Large Rivers	10^{-2} to 1	
Estuaries	1 – 20	
Lakes		
Hypolimnion	10	} Mackay [10]
Thermocline	1	
Epilimnion	3×10^5	

Surface active agents (surfactants) can reduce or inhibit volatilization. These agents form a layer one or more molecules thick on the surface of the water. The resistance of this layer is given by Smith *et al.* [19] as

$$r_s = 1/H'k_s = RT/Hk_s \quad (15-16)$$

k_s is the mass transfer coefficient at the interface and is defined as

$$k_s = \alpha \sqrt{RT/2\pi M} \quad (15-17)$$

where

- α = the accommodation coefficient, or the fraction of molecules striking the surface that condense on the surface
- R = gas constant = 8.3×10^7 ergs/mol-K
- T = temperature (K)
- M = molecular weight (g/mol)

These authors give no values for α and no method for estimating it.

The values of H for different chemicals give some insight into the controlling rate processes. Figure 15-3 postulates certain ranges of H [10,15] and presents some generalizations regarding the volatility of chemicals that fall in these ranges. (As in Figure 15-2, H is computed by Eq. 15-8 with P_{vp} in atm and S in mol/m³.)

- If H is less than about 3×10^{-7} atm-m³/mol, the substance is less volatile than water and its concentration will increase as the water evaporates. Humidity in the air reduces the volatilization rate of water somewhat, so the lower limit can be set at about 10^{-7} . The substance could be considered essentially nonvolatile.
- In the range $10^{-7} < H < 10^{-5}$ atm-m³/mol, the substance volatilizes slowly at a rate dependent on H . The gas-phase resistance dominates the liquid-phase resistance by a factor of ten at least. The rate is controlled by slow molecular diffusion through air.
- For H below about 2×10^{-5} atm-m³/mol, the pollutant tends to partition into the liquid (i.e., it is quite soluble) and the transfer is gas-phase-controlled.

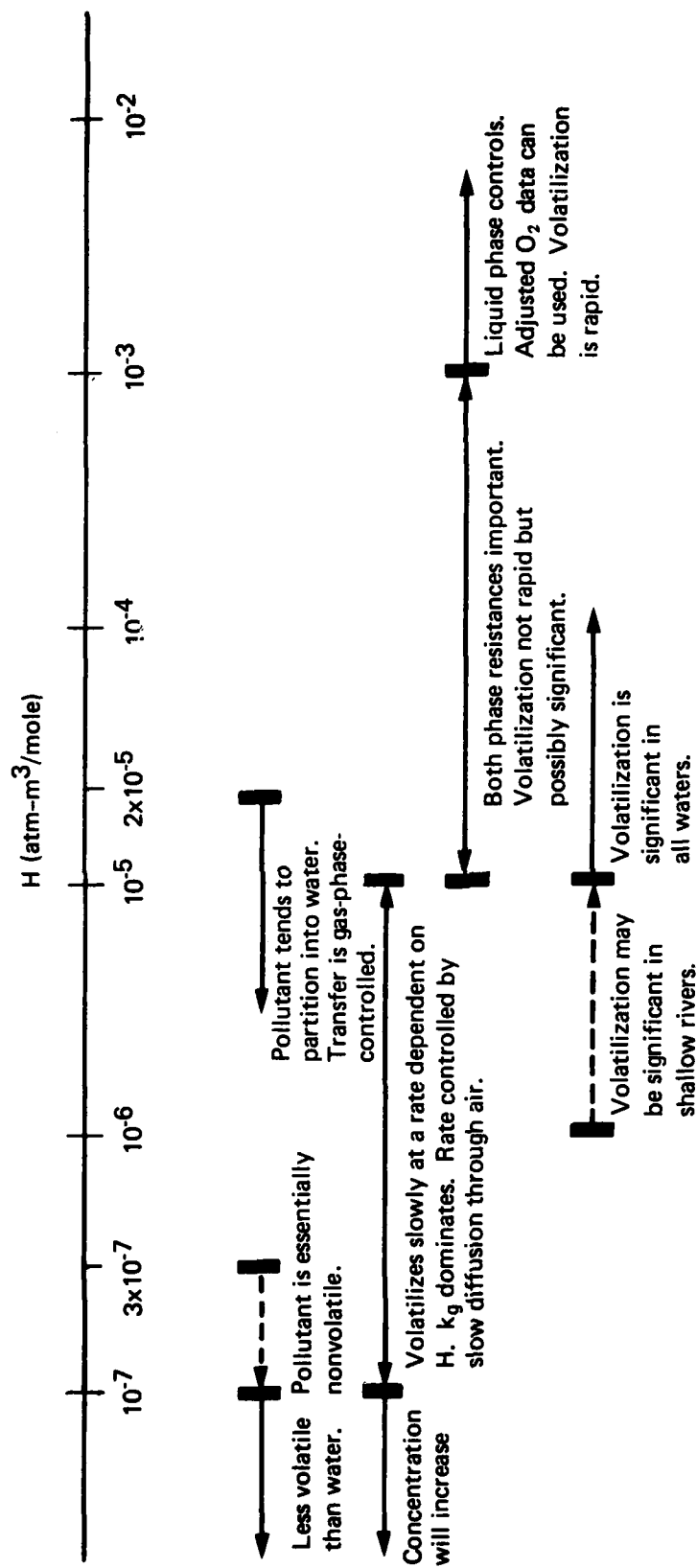


FIGURE 15-3 Volatility Characteristics Associated with Various Ranges of Henry's Law Constant

- In the range of $10^{-5} < H < 10^{-3}$ atm-m³/mol, liquid-phase and gas-phase resistances are both important. Volatilization for compounds in this range is less rapid than for compounds in a higher range of H but is still a significant transfer mechanism. Polycyclic aromatic hydrocarbons and halogenated aromatics lie in this range.
- Where H is high ($> 10^{-3}$ atm-m³/mol), the resistance of the water film dominates by a factor of at least ten. The transfer is liquid-phase-controlled. In this region $k_1 \ll Hk_g/RT$ (or $r_1 \gg r_g$), and Eq. 15-10 becomes

$$N = k_1 \left(C - \frac{P}{H} \right) \quad (15-18)$$

where the flux N is in g/cm².s and P/H is g/cm³. For most hydrocarbons that are only sparingly water-soluble (hydrophobic) and have relatively high values of the Henry's law constant, the resistance lies in the liquid phase.

If the atmospheric concentration (and thus P/H) is negligible, the transfer coefficient is independent of the value of the Henry's law constant, so the latter can be disregarded in the overall mass transfer rate equation (15-10).

Temperature affects volatilization mainly through its effect on H via its effect on vapor pressure, but it also influences k_1 through its effect on diffusivity. Since in this case the volatilization rate is independent of H , the temperature effect is slight.

Method of Smith et al. For high-volatility compounds with $H > 10^{-3}$, Smith *et al.* [18,19] have developed a method for using the oxygen reaeration rate constant to determine the first-order volatilization rate constant. They show that¹

$$k_v^c/k_v^o = K_L^c/K_L^o = d^o/d^c \approx D^c/D^o \quad (15-19)$$

where

k_v^c = overall liquid-phase exchange coefficient or first-order volatilization rate constant — chemical (hr⁻¹)

1. The relation to D^c/D^o , while not exact, is useful for estimation purposes.

- k_v^o = oxygen overall liquid-phase exchange coefficient or oxygen reaeration rate constant (hr^{-1})
 K_L^c = overall liquid-film mass transfer coefficient — chemical (hr^{-1})
 K_L^o = overall liquid-film mass transfer coefficient — oxygen (hr^{-1})
 D^c = diffusion coefficient in solution — chemical (cm^2/s)
 D^o = diffusion coefficient in solution — oxygen (cm^2/s)
 d^o = molecular diameter — oxygen (cm)
 d^c = molecular diameter — chemical (cm)

If the oxygen reaeration rate constant is known for a given water body or type of water body, it is clear from Eq. 15-19 that the volatilization rate constant can be estimated from either the ratio of diffusivities or the ratio of molecular diameters:

$$k_v^c = k_v^o (d^o/d^c) \approx k_v^o (D^c/D^o) \quad (15-20)$$

Table 15-2 compares measured and predicted values of these ratios.

TABLE 15-2

Measured Reaeration Coefficient Ratios for High-Volatility Compounds

Compound	H ($\frac{\text{atm-m}^3}{\text{mole}}$)	Measured k_v^c/k_v^o	Predicted d^o/d^c	Diffusion Coeff. Ratio D^c/D^o	Molecular Wt. Ratio (M^o/M^c) ^{0.5}
Chloroform	3.8×10^{-3}	$\left\{ \begin{array}{l} .57 \pm .02 \\ .66 \pm .11 \end{array} \right\}$.40	.47	.52
1,1-Dichloroethane	5.8×10^{-3}	$.71 \pm .11$.44	.47	.57
Oxygen	7.2×10^{-2}	1.0	1.0		
Benzo[b] thiophene	2.7×10^{-4}	$.38 \pm .08$.38		
Dibenzothiophene	4.4×10^{-4}	.14	.33		
Benzene	5.5×10^{-3}	$.57 \pm .02$.45	.64
Carbon dioxide		$.89 \pm .03$.84	.85
Carbon tetrachloride	2.3×10^{-2}	$.63 \pm .07$.43	.47
Dicyclopentadiene		$.54 \pm .02$.31	.49
Ethylene	8.6	$.87 \pm .02$.70	1.06
Krypton		$.82 \pm .08$.78	.62
Propane		$.72 \pm .01$.53	.85
Radon		$.70 \pm .08$.66	.38
Tetrachloroethylene	8.3×10^{-3}	$.52 \pm .09$.40	.44
Trichloroethylene	1×10^{-2}	$.57 \pm .15$.44	.49

Source: Smith *et al.* [18, 19]

To extend the utility of this method, Smith *et al.* [19] have measured the ratio k_v^c/k_v^o in the laboratory for several chemicals. The volatilization coefficient $(k_v^c)_{env}$ can be estimated from

$$(k_v^c)_{env} = (k_v^c/k_v^o)_{lab} (k_v^o)_{env} \quad (15-21)$$

In principle, k_v^c is the same as K_L/Z , but since k_v^c has the depth and other water-body characteristics embedded within it due to the use of k_v^o , no adjustment is required to use it directly in Eq. 15-11 or 15-12.

The ratio $(k_v^c/k_v^o)_{lab}$ was found to be independent of turbulence conditions for high-volatility compounds with $H > 6.5 \times 10^{-3} \text{ atm-m}^3/\text{mol}$. It was also found to be independent of k_v^o over the range $0.05 < k_v^o < 15 \text{ hr}^{-1}$ and independent of temperature from 4°C to 50°C .

Equation 15-21 applies particularly to rivers. For lakes and ponds, the following equation may be more accurate:

$$(k_v^c)_{env} = (k_v^c/k_v^o)_{lab}^{1.6} (k_v^o)_{env} \quad (15-22)$$

Alternatively, $(k_v^c)_{env}$ can be estimated for lakes and ponds by

$$(k_v^c)_{env} \approx (D^c/D^o) (k_v^o)_{lake} \quad (15-23)$$

and for rivers by

$$(k_v^c)_{env} \approx (D^c/D^o) (k_v^o)_{river} \quad (15-24)$$

Diffusion coefficients for compounds in water can be estimated by the following equation:²

$$D^c = \frac{14 \times 10^{-5}}{\mu_w^{1.1} / V_b^{0.6}} \quad (15-25)$$

where μ_w is the viscosity of water (cp) and V_b is the molar volume of the chemical at its normal boiling point (cm^3/mol). The value of μ_w is about 1.0 cp at 20°C .

Typical values of k_v^o in the environment are given in Table 15-3 or can be computed from the equations below. If a $(k_v^c/k_v^o)_{lab}$ value is not known, one for a similar high-volatility chemical should be a reasonable

2. Additional estimation methods are given in Chapter 17.

TABLE 15-3

Oxygen Reaeration Coefficients, $(k_v^0)_{env}$, for Water Bodies

Water Body	Literature Values (hr^{-1})	Calculated Values ^a (hr^{-1})
Pond	0.0046 – 0.0096	0.008
River	0.008, 0.04 – 0.39	0.04
Lake	0.004 – 0.013	0.01

a. From Tsivoglou [21]

Source: Smith *et al.* [19]

substitute. The values of k_v^0 for ponds and lakes are speculative and depend on depth.

For predicting reaeration rates in rivers, Møckay and Yuen [15] present the equations listed below; these correlate k_v^0 with river flow velocity, depth, and slope.

$$\text{Tsivoglou-Wallace: } k_v^0 = 638 V_{curr} s \text{ hr}^{-1} \quad (15-26)$$

$$\text{Parkhurst-Pomeroy: } k_v^0 = 1.08 (1 + 0.17 F^2) (V_{curr} s)^{0.0375} \text{ hr}^{-1} \quad (15-27)$$

$$\text{Churchill } et al.: k_v^0 = 0.00102 V_{curr}^{2.695} Z^{-3.085} s^{-0.823} \text{ hr}^{-1} \quad (15-28)$$

If no slope data are available:

$$\text{Isaacs-Gundy: } k_v^0 = 0.223 V_{curr} Z^{-1.5} \text{ hr}^{-1} \quad (15-29)$$

$$\text{Langbein-Durum: } k_v^0 = 0.241 V_{curr} Z^{-1.33} \text{ hr}^{-1} \quad (15-30)$$

where

- V_{curr} = river flow velocity (m/s)
- s = river bed slope = m drop/m run (nondimensional)
- Z = river depth (m)
- F = Froude number = V_{curr} / \sqrt{gZ} (dimensionless)
- g = acceleration of gravity = 9.8 m/s^2

Since none of the foregoing is clearly superior to the others, the best approach is probably to use all that are applicable and then average the

results.³ The values of k_g° , D° and D° are then used in Eq. 15-19 to determine k_g° .

For the range $10^{-3} < H < 10^{-2}$ atm-m³/mol, Southworth [20] developed a method for estimating the volatilization rates of polycyclic aromatic hydrocarbons (PAHs). He derived equations for estimating the phase exchange coefficients k_g and k_l from laboratory data, which are used in computing the overall liquid-phase mass transfer coefficient,

$$K_L = \frac{H'k_g k_l}{H'k_g + k_l} \text{ cm/hr} \quad (15-31)$$

For the gas-phase exchange coefficient, Southworth's equation is

$$k_g = 1137.5 (V_{\text{wind}} + V_{\text{curr}}) \sqrt{18/M} \text{ cm/hr} \quad (15-32)$$

where V_{wind} and V_{curr} are in m/s. The equation used for the liquid-phase exchange coefficient depends on the wind speed. For $V_{\text{wind}} < 1.9$ m/s,

$$k_l = 23.51 \left(\frac{V_{\text{curr}}^{0.969}}{Z^{0.673}} \right) \sqrt{32/M} \text{ cm/hr} \quad (15-33)$$

where Z is in meters. For $1.9 < V_{\text{wind}} < 5$ m/s,

$$k_l = 23.51 \left(\frac{V_{\text{curr}}^{0.969}}{Z^{0.673}} \right) \sqrt{32/M} e^{0.526(V_{\text{wind}} - 1.9)} \text{ cm/hr} \quad (15-34)$$

Estimated values of k_l and k_g from these equations are plotted in Figures 15-4 and 15-5, respectively, for a range of molecular weights and environmental parameters. They are also listed in Table 15-4 for a variety of organic compounds.

If values for the phase exchange coefficients are not available, they can be roughly estimated. For k_l , Cohen *et al.* [3] have defined three regions:

- (1) $V_{\text{wind}} < 3$ m/s
 - Water surface is relatively calm.
 - Flow is aerodynamically smooth.

3. The reaeration rate for a river 2 m deep and flowing at 1 m/s is about 0.042/hr.

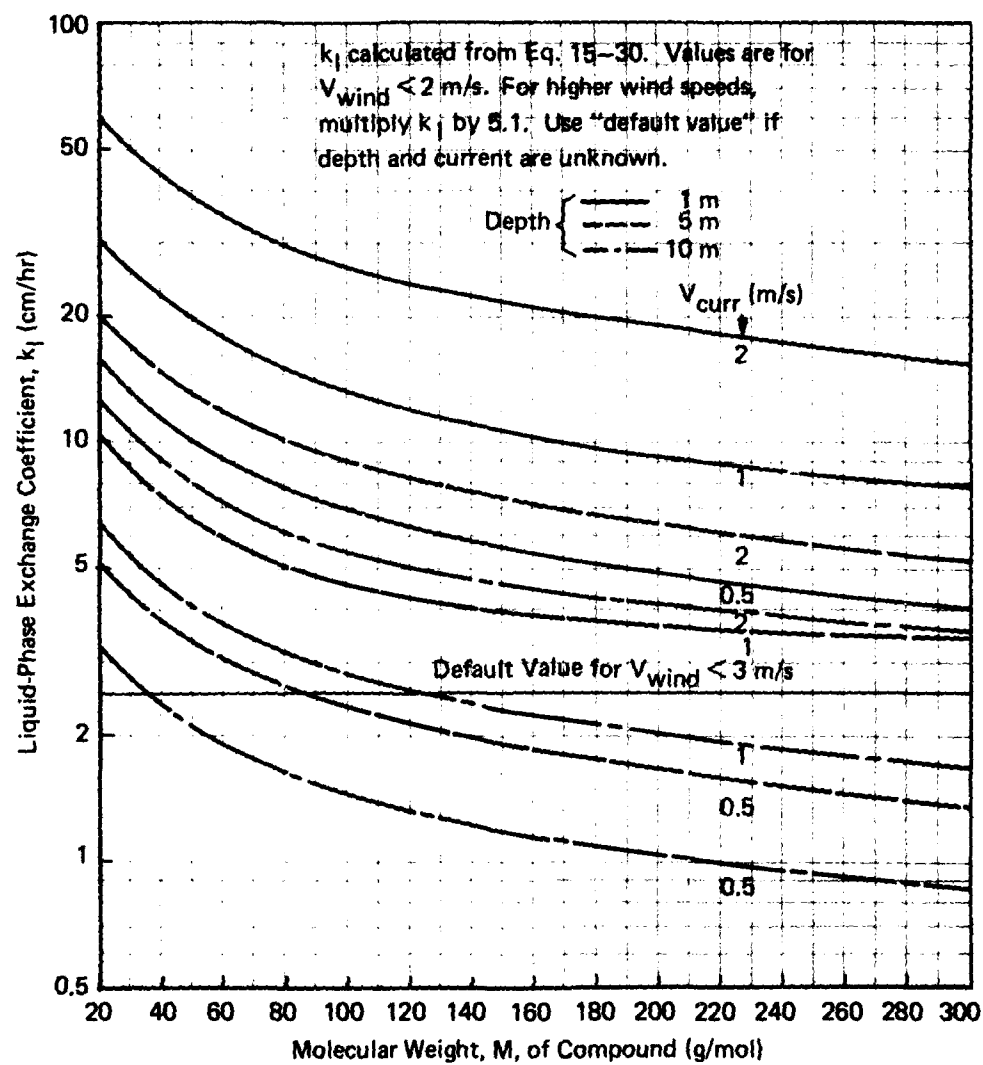


FIGURE 15-4 Effect of Molecular Weight and Environmental Characteristics on Liquid-Phase Exchange Coefficient

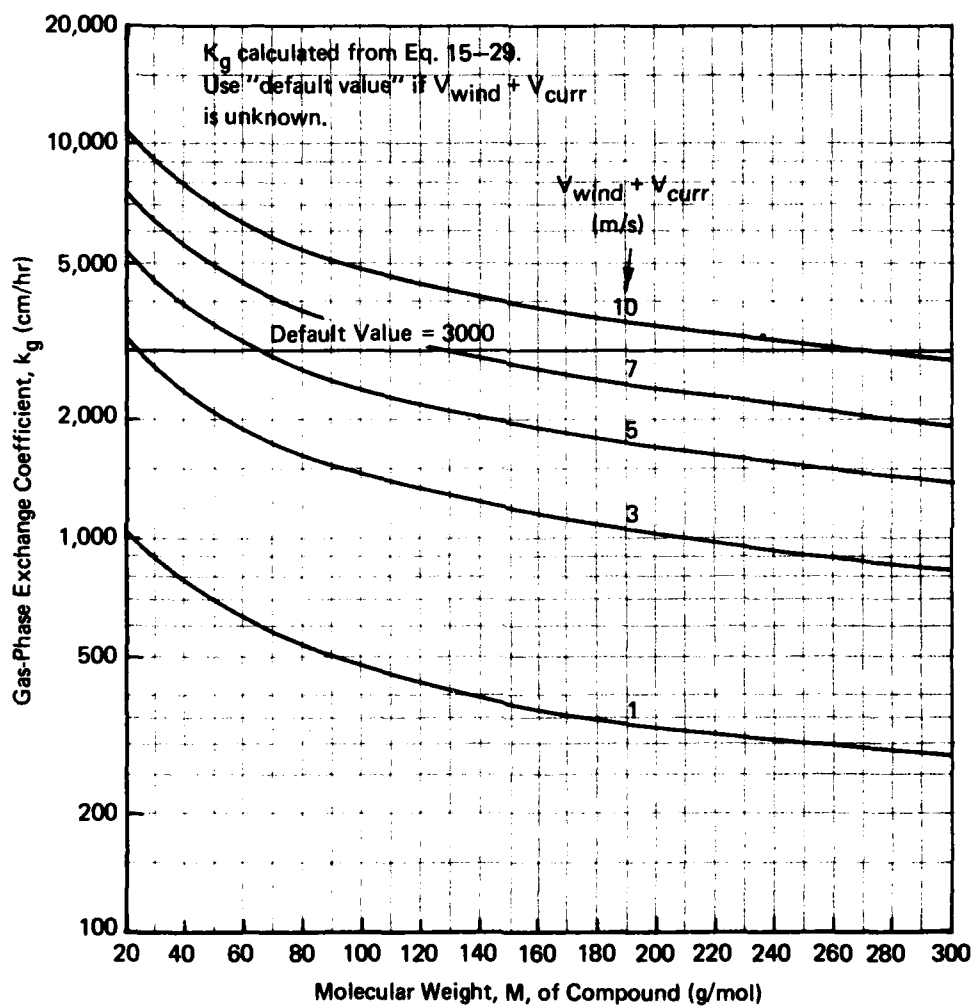


FIGURE 15-5 Effect of Molecular Weight, Wind Speed and Current on Gas-Phase Exchange Coefficient

TABLE 15-4

Volatilization Parameters for Selected Chemicals

Chemical	M (g/mol)	Solubility ^a mg/L mol/m ³	Vapor Pressure at 20°C mm Hg atm	Henry's Law Const. $\frac{H}{H'}$ (Non-dim.)	Phase Exchange Coeff. ^b (cm/hr) Liquid Gas k_l k_g	Mass Transfer Coeff. K_L (cm/hr)	Half-life, ^c $\tau_{1/2}$ (hr)
Low Volatility ($H < 3 \times 10^{-7}$)							
3-Bromo-1-propanol	139	1.7×10^{-5} 1223	0.1 1.3×10^{-4}	1.1×10^{-7} 4.6×10^{-6}	16 1600	7.4×10^{-3}	9400
Dieldrin	381	0.25 6.6×10^{-4}	1×10^{-7} 1.3×10^{-10}	2×10^{-7} 8.9×10^{-6}	12 990	8.8×10^{-3}	7840
Middle Range ($3 \times 10^{-7} < H < 10^{-3}$)							
Lindane	290.9	7.3 2.5×10^{-2}	9.4×10^{-6} 1.2×10^{-8}	4.8×10^{-7} 2.2×10^{-5}	14 1130	0.025	2760
m-Bromonitrobenzene	170	10^4 58.8	0.07 9.2×10^{-5}	1.6×10^{-6} 7.4×10^{-5}	16 1500	0.11	626
Pentachlorophenol	266	14 5.3×10^{-2}	1.4×10^{-4} 1.8×10^{-7}	3.4×10^{-6} 1.5×10^{-4}	12 1150	0.17	406
4-t-Butylphenol	150	10^3 6.7	0.046 6.1×10^{-5}	9.1×10^{-6} 3.8×10^{-4}	17 1600	0.59	117
Triethylamine	101	7.3×10^4 723	7.0 9.2×10^{-3}	1.3×10^{-5} 5.4×10^{-4}	22 1900	0.98	7
Aldrin	365	0.2 5.5×10^{-4}	6×10^{-6} 7.9×10^{-9}	1.4×10^{-5} 6.1×10^{-4}	12 1810	1.0	68
Nitrobenzene	123	2×10^3 16.3	0.27 3.5×10^{-4}	2.2×10^{-5} 9.3×10^{-4}	20 1700	1.5	45
Epichlorohydrin	92.5	6.6×10^4 711	17.3 2.3×10^{-2}	3.2×10^{-5} 1.3×10^{-3}	24 2000	2.3	29
DDT	354.5	1.2×10^{-3} 3.4×10^{-6}	1×10^{-7} 1.3×10^{-10}	3.8×10^{-5} 1.7×10^{-3}	13 1025	1.5	45
Phenanthrene	178	1.29 7×10^{-3}	2.1×10^{-4} 2.8×10^{-7}	3.9×10^{-5} 1.7×10^{-3}	18 1450	2.2	31
Acenaphthene	154	3.9 2.5×10^{-2}	2.8×10^{-3} 3.7×10^{-6}	1.5×10^{-4} 6.2×10^{-3}	19 1560	6.4	11
Acetylene tetrabromide	344	650 1.9	0.3 3.9×10^{-4}	2.1×10^{-4} 8.9×10^{-3}	13 1000	5.3	13.1
Aroclor 1242	254	0.24 9.5×10^{-4}	4.1×10^{-4} 5.3×10^{-7}	5.6×10^{-4} 2.4×10^{-2}	15 1210	9.9	7
Ethylene dibromide	188	4.3×10^3 22.9	11.6 1.5×10^{-2}	6.6×10^{-4} 2.8×10^{-2}	16 1400	11.4	6.1

(continued)

TABLE 15-4 (Continued)

Chemical	M (g/mol)	Solubility ^a mg/L	Solubility ^a mol/m ³	Vapor Pressure at 20°C mm Hg	atm	Henry's Law Const. $\frac{H}{H'}$ (Non-dim.)	Phase Exchange Coeff. $\frac{b}{b'}$ (cm/hr) Liquid k_l Gas k_g	Mass Transfer Coeff. K_L (cm/hr)	Half-life, c $\tau_{1/2}$ (hr)
High Volatility ($H > 10^{-3}$)									
Ethylene dichloride	99	8.0×10^3	80.8	67	0.09	1.1×10^{-3}	4×10^{-2}	17.1	4
Naphthalene	128	33	0.26	0.23	3×10^{-4}	1.15×10^{-3}	4.9×10^{-2}	16.9	4.1
Biphenyl	154	7.5	0.05	0.06	7.5×10^{-5}	1.5×10^{-3}	6.8×10^{-2}	16.2	4.3
Aroclor 1254	326	1.2×10^{-2}	3.7×10^{-5}	7.7×10^{-5}	1×10^{-7}	2.7×10^{-3}	1.2×10^{-1}	13	1070
Methylene chloride	85	1.3×10^4	155	349	0.46	3×10^{-3}	1.3×10^{-1}	25	2000
Aroclor 1248	292	0.054	1.85×10^{-4}	4.9×10^{-4}	6.5×10^{-7}	3.5×10^{-3}	1.6×10^{-1}	14	1130
Chlorobenzene	113	472	4.2	11.8	1.6×10^{-2}	3.7×10^{-3}	1.65×10^{-1}	22	1820
Chloroform	119	8×10^3	67	246	0.32	4.8×10^{-3}	2.0×10^{-1}	20	1700
o-Xylene	106	175	1.7	6.6	8.7×10^{-3}	5.1×10^{-3}	2.2×10^{-1}	23	1870
Benzene	78	1780	22.8	95.2	1.25×10^{-1}	5.5×10^{-3}	2.4×10^{-1}	27	2180
Toluene	92	515	5.6	28.4	3.7×10^{-2}	6.6×10^{-3}	2.8×10^{-1}	25	2010
Aroclor 1260	361	2.7×10^{-3}	7.5×10^{-6}	4.1×10^{-5}	5.3×10^{-8}	7.1×10^{-3}	3.0×10^{-1}	13	1020
Perchloroethylene	166	400	2.4	14.3	2×10^{-2}	8.3×10^{-3}	3.4×10^{-1}	17	1450
Ethyl benzene	106	152	1.43	9.5	1.25×10^{-2}	8.7×10^{-3}	3.7×10^{-1}	23	1870
Trichloroethylene	131	1×10^3	7.6	60	8×10^{-2}	1×10^{-2}	4.2×10^{-1}	21	1700
Mercury	201	3×10^{-2}	1.5×10^{-4}	1.3×10^{-3}	1.7×10^{-6}	1.1×10^{-2}	4.8×10^{-1}	17	1360
Methyl bromide	95	1.3×10^4	137	1.4×10^3	1.8	1.3×10^{-2}	5.6×10^{-1}	23	2000
Cumene (isopropyl benzene)	120	50	0.416	4.6	6.1×10^{-3}	1.5×10^{-2}	6.2×10^{-1}	22	1760
1,1,1-Trichloroethane	133	950	7.1	100	0.13	1.8×10^{-2}	7.7×10^{-1}	19	1650
Carbon tetrachloride	154	800	5.2	91	0.12	2.3×10^{-2}	9.7×10^{-1}	19	1500
Methyl chloride	50.5	7.4×10^3	146	3.6×10^3	4.74	2.4×10^{-2}	3.6×10^{-1}	30	2600
Ethyl chloride	109	900	8.3	460	6.1×10^{-1}	7.3×10^{-2}	3.1	22	1800
Vinyl chloride	62.5	90	1.44	2580	3.4	2.4	99	28	2400
2,2,4-Trimethyl pentane	114	2.44	2.1×10^{-2}	49.3	6.5×10^{-2}	3.1	129	22	1810
n-Octane	114	0.66	5.8×10^{-3}	14.1	1.85×10^{-2}	3.2	136	22	1810
Fluorotrichloromethane	137					5.0		11.3	1090
Ethylene	28	131	4.7	> 40		> 8.6	~ 360	40	3700

a. Sources: Refs. 11, 13, 14, 22

b. From Eqs. 15-32 to -34 and Figs. 15-4 and -5,

using $V_{wind} = 3\text{m/s}$ and $V_{curr} = 1\text{m/s}$ c. From Eq. 15-12, with $Z = 1\text{m}$

- k_1 values are typically 1-3 cm/hr and appear to be strongly influenced by mixing originating from within the water body.
 - Wind velocity in this range has no apparent effect on the value of k_1 .
 - A suggested value for k_1 is 2-3 cm/hr.
 - The mass transfer rate is dominated by the underlying hydrodynamics, which are very site-specific and dependent on recent environmental conditions.
- (2) $3 \text{ m/s} < V_{\text{wind}} < 10 \text{ m/s}$
- k_1 increases from 3.5 to 30 cm/hr.
 - In the range of 3-6 m/s, the increase in k_1 is attributable to the onset of ripples and an increase in surface roughness.
 - Above 6 m/s, wave growth is appreciable. Flow becomes completely rough, which increases the rate of mass transfer appreciably.
- (3) $10 \text{ m/s} < V_{\text{wind}}$
- Waves may begin to break.
 - k_1 increases due to greater surface area, spray, bubble entrainment, and disintegration of wave crests.
 - k_1 values can reach 70 cm/hr.

Liss and Slater [9] give values of k_1 for several gases and suggest that 20 cm/hr is appropriate for the sea surface. This value should be applicable for gases of $15 < M < 65$; outside this range, k_1 can be adjusted by multiplying by the square root of the ratio of the molecular weight of CO_2 to that of the other gas, i.e.,

$$k_1 = 20 \sqrt{44/M} \text{ cm/hr} \quad (15-35)$$

The correction is not well established in extending data for low-molecular-weight gases to high-molecular-weight compounds such as PCBs.

The ratio k_g/k_1 ranges from about 50 to 200 [10]. Liss and Slater [9] suggest a value of about 96 for oceans. For the transfer of water vapor from the ocean surface, they give a value of about 3000 cm/hr for k_g . The value of k_g for some other compound can be estimated by multiplying 3000 by the square root of the ratio of the molecular weights:

$$k_g = 3000 \sqrt{18/M} \text{ cm/hr} \quad (15-36)$$

There is evidence that the phase exchange coefficients for transfer across the air-sea interface may be too high for lakes and other smaller bodies of water [17].

Basic Steps of Calculation. The following data are the minimum required for calculating rates of vaporization:

- Chemical properties — vapor pressure, aqueous solubility, molecular weight.⁴
 - Environmental characteristics — wind speed, current speed, depth of water body.
- (1) Find Henry's law constant (H) from Eq. 15-8 and/or Figure 15-2.
 - (2) If $H < 3 \times 10^{-7}$, volatilization can be considered unimportant as an inter-media transfer mechanism, and no further calculations are necessary.
 - (3) If $H > 3 \times 10^{-7}$, the chemical can be considered volatile. Determine the nondimensional Henry's law constant, $H' = H/RT$ ($RT = 0.024$ at 20°C).
 - (4) Compute the liquid-phase exchange coefficient (k_l). For a compound of low molecular weight (< 65), use Eq. 15-35. If $M > 65$, use Eq. 15-33 for $V_{\text{wind}} < 1.9$ m/s or Eq. 15-34 for $1.9 < V_{\text{wind}} < 5$ m/s. Alternatively, obtain the approximate value of k_l from Figure 15-4.
 - (5) Compute the gas-phase exchange coefficient (k_g). For a compound of low molecular weight (< 65), use Eq. 15-36; if $M > 65$, use Eq. 15-32. Alternatively, read the approximate value of k_g from Figure 15-5.
 - (6) If the necessary data are available, compute the surfactant-resistance mass transfer coefficient (k_s), using Eq. 15-17.
 - (7) Compute overall liquid-phase mass transfer coefficient, K_L . If just the gas-phase and liquid-phase resistances are to be considered, use Eq. 15-31 or (if the dimensional Henry's law constant is used) the following equation, which is a rearrangement of Eq. 15-9:

$$K_L = \frac{(H/RT)k_g k_l}{(H/RT)k_g + k_l} \text{ cm/hr}$$

4. Estimation methods for aqueous solubility and vapor pressure are given in Chapters 2 and 14, respectively.

If resistances other than those of the gas and liquid phases must be considered, they can be included here (see Eqs. 15-13 and 15-16).

$$R_L = 1/K_L, r_1 = 1/k_1, r_g = 1/H'k_g = RT/Hk_g, r_w = \tau_D/Z = Z/1.3 D_z$$

$$r_s = 1/H'k_s = RT/Hk_s$$

and

$$R_L = r_1 + r_g + r_w + r_s$$

or

$$1/K_L = 1/k_1 + 1/H'k_g + Z/1.3 D_z + 1/H'k_s$$

- (8) Compute the half-life ($\tau_{1/2}$) from the above value of K_L and the depth of the water (Z), using Eq. 15-12.

Example 15-1: A High-Volatility Chemical Estimate the half-life of trichloroethylene at 20°C in a river 1 meter deep flowing at 1 m/s and with a wind velocity of 3 m/s. The vapor pressure of this compound is 0.08 atm, its molecular weight is 131 g/mol, and its solubility is 1.1 g/L (8.4 mol/m³).

- (1) Calculate the Henry's law constant from Eq. 15-8.

$$H = 0.08/8.4 = 0.01 \text{ atm-m}^3/\text{mol}$$

- (2) Since $H > 10^{-3}$ atm-m³/mol, trichloroethylene is highly volatile.

- (3) Calculate the nondimensional Henry's law constant:

$$H' = 0.01/0.024 = 0.42 \text{ (at 20°C)}$$

- (4) Compute the liquid-phase exchange coefficient, k_1 . Since $M > 65$ and $1.9 < V_{\text{wind}} < 5$, Eq. 15-34 is used.

$$k_1 = 23.51(1^{0.969} / 1^{0.673}) \sqrt{32/131} e^{0.526(3-1.9)} \\ = 21 \text{ cm/hr}$$

- (5) Compute the gas-phase exchange coefficient, k_g , from Eq. 15-32.

$$k_g = 1137.5(3+1) \sqrt{18/131} = 1700 \text{ cm/hr}$$

- (6) Use Eq. 15-31 to find the overall liquid-phase mass transfer coefficient, K_L . (It is assumed that the gas and liquid phases account for the only important resistance.)

$$K_L = \frac{0.42 \times 1700 \times 21}{(0.42)(1700) + 21} = 20.4 \text{ cm/hr}$$

- (7) Use Eq. 15-12 to find the half-life.

$$\tau_{1/2} = 0.69(100/20.4) = 3.4 \text{ hr}$$

Alternatively, by the reaeration coefficient method:

- (1) Calculate the oxygen reaeration rate constant by Eqs. 15-29 and -30. (Eqs. 15-26, -27, and -28 are not usable, because the slope of the river bed is unknown in this example.)

$$(k_v^0)_{\text{env}} = 0.223(1)(1)^{-1.5} = 0.223 \text{ hr}^{-1}$$

and

$$(k_v^0)_{\text{env}} = 0.241(1)(1)^{-1.33} = 0.241 \text{ hr}^{-1}$$

The average of these values is about 0.23 hr^{-1} . This is within the range listed in Table 15-3 ($0.008 - 0.39 \text{ hr}^{-1}$).

- (2) The laboratory-measured value of k_v^c/k_v^0 (see Table 15-2) is 0.57 ± 0.15 . Therefore, by Eq. 15-21,

$$(k_v^c)_{\text{env}} = 0.57(0.23) = 0.13 \text{ hr}^{-1}$$

For comparison, the rate constant corresponding to the value of K_L found in the preceding method is $K_L/Z = 20/100 = 0.2 \text{ hr}^{-1}$.

- (3) Using Eq. 15-12,

$$\begin{aligned} \tau_{1/2} &= 0.69(Z/K_L) = 0.69(k_v^c)^{-1} \\ &= 5.8 \text{ hr} \end{aligned}$$

This agrees fairly well with the 3.4-hour half-life found by the preceding method.

Example 15-2: A Medium-Volatility Chemical Estimate the half-life of acenaphthene under the same environmental conditions as in Example 15-1. Given: $P_{vp} = 3.72 \times 10^{-6} \text{ atm}$, $M = 154 \text{ g/mol}$, $S = 3.9 \text{ mg/L} = 0.025 \text{ mol/m}^3$.

- (1) From Eq. 15-8,

$$H = 3.72 \times 10^{-6} / 0.025 = 1.5 \times 10^{-4} \text{ atm-m}^3/\text{mol}$$

- (2) Since $10^{-5} < H < 10^{-3} \text{ atm-m}^3/\text{mol}$, acenaphthene is of medium volatility.

- (3) Calculate the nondimensional Henry's law constant:

$$H' = H/RT = \frac{1.5 \times 10^{-4}}{0.024} = 6.2 \times 10^{-3} \text{ at } 20^\circ\text{C}$$

- (4) Compute the liquid-phase exchange coefficient, k_l . Since $M > 65$ and $1.9 < V_{\text{wind}} < 5$, Eq. 15-34 is used.

$$k_l = 23.51 (1^{0.969} / 1^{0.673}) \sqrt{32/154} e^{0.526 (3-1.9)} \\ = 19.1 \text{ cm/hr}$$

- (5) Compute the gas-phase exchange coefficient, k_g , from Eq. 15-32.

$$k_g = 1137.5 (3+1) \sqrt{18/154} = 1560 \text{ cm/hr}$$

- (6) Use Eq. 15-31 to find the overall liquid-phase mass transfer coefficient, K_L . (It is assumed that the gas and liquid phases account for the only important resistances.)

$$K_L = \frac{(6.2 \times 10^{-3}) (1560) (19.1)}{(6.2 \times 10^{-3}) (1560) + 19.1} = \frac{185}{28.8} = 6.4 \text{ cm/hr}$$

- (7) Use Eq. 15-12 to find the half-life.

$$\tau_{1/2} = 0.69 (100/6.4) = 11 \text{ hr}$$

Basic Steps of Calculation via Reaeration Coefficient. For a high-volatility chemical, the volatilization rate constant can be estimated by the reaeration coefficient method. The following data are required:

- $(k_v^c/k_v^o)_{lab}$ or the ratio of diffusion coefficients D^c/D^o or the ratio of molecular diameters d^o/d^c ;
- $(k_v^o)_{env}$ or stream flow parameters (velocity, stream bed slope, depth).

- (1) Find the oxygen reaeration coefficient, $(k_v^o)_{env}$, from Table 15-3, or compute it from Eqs. 15-26 to 15-30. (It is recommended that k_v^o be computed from all the appropriate equations and an average be taken.)
- (2) If $(k_v^c/k_v^o)_{lab}$ is known, calculate $(k_v^c)_{env}$ by Eq. 15-21 and use this value to find the half-life by Eq. 15-12.
- (3) If molecular diameters or molecular diffusivities are known, calculate $(k_v^c)_{env}$ with Eq. 15-20 and then use Eq. 15-12 to find $\tau_{1/2}$.
- (4) If neither (2) nor (3) is applicable, compute diffusivities for the chemical and oxygen via Eq. 15-25 and proceed as in step (3). (See Chapter 17 for other estimation methods.)

Example 15-3: A Low-Volatility Chemical Estimate the half-life of dieldrin in the same environment as in Example 15-1. Given: $P_{vp} = 1.3 \times 10^{-10}$ atm, $M = 381$ g/mol, $S = 0.25$ mg/L = 6.6×10^{-4} mol/m³.

(1) From Eq. 15-8,

$$H = 1.3 \times 10^{-10} / 6.6 \times 10^{-4} = 2.0 \times 10^{-7} \text{ atm-m}^3/\text{mol}$$

(2) Since the Henry's law constant is less than 3×10^{-7} , volatilization is unimportant as a transfer mechanism for dieldrin, and further calculations are unnecessary.

15-6 SYMBOLS USED⁵

C	=	concentration (M/L^3)
C_g	=	well-mixed concentration in gas phase (M/L^3)
C_l	=	well-mixed concentration in liquid phase (M/L^3)
C_o	=	initial concentration (M/L^3)
C_{sg}	=	concentration in gas phase at interface (M/L^3)
C_{sl}	=	concentration in liquid phase at interface (M/L^3)
ΔC	=	concentration difference (M/L^3)
D	=	diffusion coefficient (L^2/T)
D_L	=	longitudinal value of turbulent diffusivity in Eq. 15-14 (L^2/T)
D_z	=	perpendicular value of turbulent diffusivity in Eq. 15-14 (L^2/T)
d	=	molecular diameter (L)
F	=	Froude number
g	=	acceleration of gravity (L/T^2)
H	=	Henry's law constant (atm-m ³ /mol)
H'	=	nondimensional Henry's law constant = C_{sg}/C_{sl} or H/RT
K_G	=	overall gas-phase mass transfer coefficient (L/T)
K_L	=	overall liquid-phase mass transfer coefficient (L/T)
k	=	first-order rate constant (T^{-1})
k_g	=	gas-phase exchange coefficient (L/T)
k_l	=	liquid-phase exchange coefficient (L/T)
k_s	=	mass transfer coefficient at interface for surfactants (L/T)

5. M , L , and T indicate mass, length, and time units respectively.

k_v	=	volatilization rate constant (T^{-1})
M	=	molecular weight (g/mol)
N	=	flux (M/L^2T)
P	=	partial pressure (atm or mm Hg)
P_{vp}	=	vapor pressure of compound (atm or mm Hg)
R	=	gas constant = 8.2×10^{-5} atm-m ³ /mol-K or 8.3×10^7 ergs/mol-K
R_L	=	overall liquid-phase resistance (T/L)
r_g	=	gas-phase resistance (T/L)
r_l	=	liquid-phase resistance (T/L)
r_s	=	surfactant resistance (T/L)
r_w	=	bulk water body resistance (T/L)
S	=	aqueous solubility or saturation concentration (mol/m ³ or M/L^3)
s	=	slope of river bed (L/L)
T	=	temperature (K or °C)
t	=	time (T)
V_b	=	molar volume of chemical at normal boiling point (L^3/mol)
V_{curr}	=	current speed (L/T)
V_{wind}	=	wind speed (L/T)
Z	=	average or mean water body depth (L)
z	=	layer thickness (L)

Greek

α	=	accommodation coefficient, or fraction of molecules striking the surface that condense on the surface
μ_w	=	viscosity of water (centipoise) ≈ 1.0 cp at 20°C
$\tau_{1/2}$	=	half-life (T)
τ_D	=	half-life for turbulent diffusion (T)

Subscripts

env	=	environmental value
lab	=	laboratory value

Superscripts

c	=	chemical
o	=	oxygen

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16

VOLATILIZATION FROM SOIL

Richard G. Thomas

16-1 INTRODUCTION

Volatilization is the process by which a compound evaporates in the vapor phase to the atmosphere from another environmental compartment. Volatilization may be an important mechanism for the loss of chemicals from the soil and transfer to the air. In the case of spills or purposeful application, for example, it may be useful to know how long the compounds will persist in the soil, and volatilization is one of the factors on which persistence depends. This chapter presents methods to estimate the volatilization of a chemical from the soil to the air. Most of these methods are mathematical descriptions of the physical process of volatilization and do not generate a single number or parameter that represents a volatilization rate. These methods and descriptions will be referred to as the volatilization models.

To estimate concentrations in the soil column and/or flux of chemicals from the soil to the air, the models require as input data several chemical and environmental parameters, which must be obtained by the user. Some of the models are complex; therefore, a programmable calculator is useful for working with them.

The rate at which a chemical volatilizes from soil is affected by many factors, such as soil properties, chemical properties, and environmental conditions. These factors are discussed in the literature primarily in

terms of their effect on the evaporation of pesticides, because most previous studies of volatilization rates have concentrated on these chemicals. Other than their use, there is apparently little that distinguishes pesticides from other organics; therefore, we assumed in this chapter that the observations based on pesticides are applicable to organic chemicals in general.

A rate constant for volatilization is not a feature of the models, except in the special case of volatilization of a surface-applied chemical. For cases in which the chemical is incorporated into the soil, methods are discussed which predict the concentration in the soil as a function of time or which predict the rate of evaporation.

The methods presented here do not explicitly address all the many factors influencing volatilization from soil and may exclude certain processes for the sake of analytical tractability. Thus, the results are not extremely accurate and should be considered only generally indicative of the actual environmental behavior. Measured values are given, where available, to indicate the accuracy of the different methods.

A discussion of the volatilization process and important factors affecting the volatilization of a chemical from the soil follows this introduction. Next, the available models developed to estimate concentrations of chemicals in the soil and the flux of chemicals from the soil to the air are presented and discussed. The final main section of this chapter considers the selection of the model most applicable to the user's needs.

16-2 FACTORS AFFECTING THE VOLATILIZATION PROCESS

Properties on which Volatilization is Dependent. Chemical, soil, and general environmental properties affect volatilization. Some of the properties of a chemical involved in volatilization are its vapor pressure, solubility in water, basic structural type, and the number, kind, and position of its basic functional groups [6]. Subtle differences in chemical structure can cause a large change in vapor pressure; they can also affect the charge on a molecule, causing it to sorb on soil more or less strongly than a similar compound [6]. This can determine the fraction of compound in the soil that will volatilize. Other factors affecting volatilization rate are: compound concentration in the soil, soil water content, airflow rate over the surface, humidity, temperature, sorptive and diffusion characteristics of the soil, and bulk properties of the soil such as organic matter content, porosity, density, and clay content. All of these factors affect the distribution of a compound between the soil, soil water, soil air, and atmosphere.

The above factors can be grouped into three categories: (1) those which affect movement away from the evaporating surface into the atmosphere, (2) those which affect the vapor density (concentration of the compound in air) of the chemical, and (3) those which control the rate of movement to the evaporating surface [19]. All of the processes and factors described below fall into one or another of these categories.

Compound Distribution and Equilibria. A compound in the soil may be partitioned between the soil water, soil air, and the soil constituents. Considered as a whole, the soil represents all three phases of matter rather than one, as does the atmosphere or water. The atmosphere constitutes another air compartment which is distinct from the soil air. The rate of volatilization of an organic molecule from a sorption site on the solid phase in the soil (or in solution in the soil water) to the vapor phase in soil air and then to the atmosphere is dependent on many physical and chemical properties of both the chemical and the soil and on the process of moving from one phase to another. (These properties and processes are discussed more fully below.) The three main distribution or transport processes involved are:

- Compound in soil \leftrightarrow Compound in solution
- Compound in solution \leftrightarrow Compound in vapor phase in soil air
- Compound in vapor phase in soil air \rightarrow Compound in atmosphere

Partitioning of a chemical among the three phases can be estimated from either vapor-phase or solution-phase desorption isotherms [16].

Adsorption. Adsorption reduces the chemical activity below that of the pure compound and affects the vapor density and the volatilization rate [18]. Sorption may be a result of chemical adsorption (coulombic forces), physical adsorption (Van der Waals forces), or hydrogen bonding [6]. The concentration of the compound present in a desorbed state in solution in the soil water, along with other properties, controls the vapor density of the compound in soil air. The vapor density is directly related to the volatilization rate. The vapor density has also been shown to be inversely related to both the surface area of the soil particles and the organic matter content in the soil [6]. This follows, since sorption is usually directly related to the available surface area and organic matter content, and sorption reduces the amount of compound available to partition between the water and air.

Vapor Density. Vapor density is the concentration of a chemical in the air, the maximum concentration being a saturated vapor. The vapor density of a compound in the soil air ultimately determines the volatilization rate.

Vapor density and vapor pressure are affected by interaction with soils [16]. Some chemicals require only a low total soil concentration to have a saturated vapor in moist soil; thus, weakly adsorbed compounds may volatilize rapidly, especially if applied only to the soil surface. If the chemicals are incorporated into the soil, the concentration at the evaporating surface of the soil particles is reduced and the total volatilization rate decreases [19].

Spencer [16] found that the vapor density of dieldrin in several types of soils increased linearly with concentration but was inversely related to the organic matter content and was relatively independent of clay content when sufficient water was present to cover the surfaces. As mentioned above, even a low soil-water content increases the vapor density of the compound in the soil air by displacing it from soil surfaces. The effective vapor pressure may differ from the vapor pressure of the chemical itself because of adsorption on the soil or other matter, solution in the soil water, or retreat into deeper capillary spaces [19].

Water Content of the Soil. Water content also affects volatilization losses by competing for adsorption sites on the soil [6,16]. For non-polar and weakly polar compounds, water is preferentially sorbed onto soil particles and can displace the chemical. As most pesticides are relatively insoluble in water, a soil-water adsorption isotherm can be used to estimate concentrations in the soil/soil-water system [16]. The determination of these isotherms may be difficult, and not all compounds behave similarly; some compounds are strongly adsorbed as cations on soils, whereas others are weakly adsorbed on soils and are easily displaced by water. Between these two extremes the degree of adsorption is dependent on the polarity of the compound, which in turn may be dependent on pH and other factors [16]. For weakly polar or nonionic pesticides the fraction of soil organic matter is the most important soil factor in adsorption. Since most of the more volatile pesticides are nonionic or only weakly polar, their adsorption by soils is closely related to organic matter content [18]. Once the soil surfaces are saturated with just a molecular layer of water, the vapor density of a weakly polar compound in the soil air is greatly increased, and additional soil water does not influence the tendency of the compound to leave its sorbed site. The quantity of water required to achieve a monomolecular layer is about 2.8% in a Gila silt loam [17,19,21].

The concept of "co-distillation," in which a compound is assumed to evaporate along with the soil moisture in the same ratio as they are present in the soil/soil-water system, is not applicable. Chemicals in the soil do not behave in this manner. The loss of a compound in the presence of water is not due to co-distillation. When the water evaporates, the compound sorbs onto dry soil. Volatilization of the compound is enhanced by the *presence* of water, not its evaporation [16]. Compound loss becomes insignificant when water loss decreases, because the vapor density is reduced by adsorption on the dry soil. Conversely, the presence of water causes desorption of the compound, increasing vapor density.

As a consequence of this behavior, a compound may hold very strongly on a dry soil, thereby reducing its volatilization rate; but when the soil is wetted, the stronger affinity of the water displaces the compound, allowing volatilization to occur at a faster rate. Keeping the soil dry will reduce or stop the volatilization of some chemicals, since the soil needs some moisture for the displacement or solubilization of the chemical [6]. However, if the concentration of a compound in soil becomes high enough that its chemical activity approaches that of the pure compound, the presence or absence of water will not affect its volatilization rate.

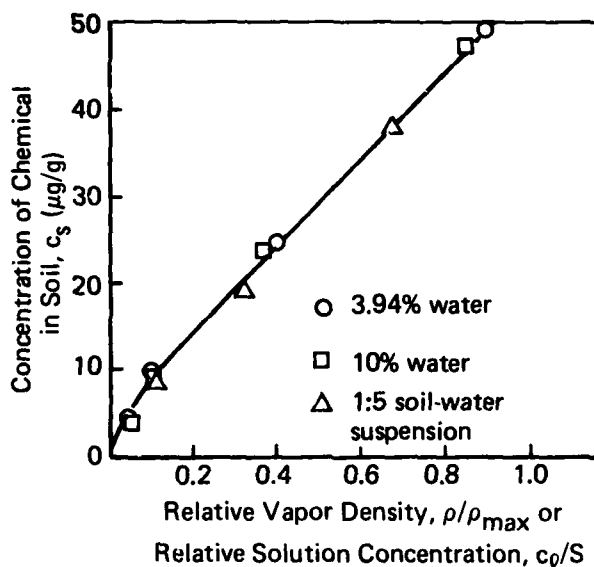
Partitioning between Water, Soil, and Air. The concentration of a compound in the soil water can be determined from sorption and solution equilibria. These equilibria depend on the soil, the chemical, and the interaction with water [16]. The vapor density in the air in equilibrium with the soil solution can be determined from Henry's law regardless of solubility or volatility [16].

Desorption isotherms relating compound adsorbed by the soil to relative vapor density and to relative solution concentration (Figure 16-1) were all the same for lindane [17]. These relationships indicate that, for a compound that is relatively insoluble in water and weakly polar, the quantity that must be adsorbed to create a saturated solution is the same as that required for a saturated vapor; at higher soil concentrations the air is saturated with the vapor [17]. These observations would probably hold for most compounds regardless of their solubilities, although more soluble compounds may not exhibit linear vapor density/solution concentration isotherms over a wide concentration range [16].

The relationships between the equilibrium concentrations for each soil component¹ — soil solids (c_s), soil water (c_w/S), and soil air

1. See §16-6 for symbol definitions.

(ρ/ρ_{\max}) — will probably not change with varying water: soil ratios over the usual field soil water content range; as the water content decreases, however, the compound concentration in solution, and hence vapor density, increases. The equilibrium shifts to a higher amount of compound adsorbed, as shown in Figure 16-1.



Source: Spencer [16]

FIGURE 16-1 Desorption Isotherms for Lindane

The change in concentration in the soil solid phase with a change in soil water content is greater with more soluble compounds, since a greater proportion of the total compound in the soil is in solution at any time. As a general rule, for compounds that can be displaced by water, the higher the sorption partition coefficient (c_s/c_0), the less is the effect of changing water content on solution concentrations and vapor densities within the "wet" soil moisture range above one monolayer of water [16].

Temperature. The effect of temperature on the volatilization process is unpredictable. The primary effect is on vapor density: an increase in temperature normally increases the equilibrium vapor density, which in turn increases the volatilization rate [6]. However, complicating factors can alter the expected result. Spencer [16] discusses experiments with lindane in which increasing temperature resulted in a lower relative vapor density (ρ/ρ_{\max}). This ratio should have remained constant if changes in solubility or vapor density were the only operant effects. In

this instance, adsorption reduced the rate of increase of ρ relative to ρ_{\max} . Lindane adsorption appears to be a net endothermic process that results in a decrease in free energy and an increase in entropy, the opposite of the usual results. Thus, an increase in temperature will not necessarily lead to an increase in volatilization.

Low temperature may not eliminate volatilization entirely, since diffusion may continue even in frozen soil [7]. The likely explanation for this phenomenon is that water near clay surfaces is subject to attractive forces that prevent it from assuming the crystalline structure of ice, which would inhibit diffusion. This effect has not been demonstrated for many organic chemicals in soil; there is a general lack of data on the temperature effect for organic chemicals.

Atmospheric Conditions. Air flow over the soil surface plays an important role in the volatilization process. The evaporation rate is determined by the diffusion of vapor into the surrounding air. Close to the surface (i.e., in the boundary layer) there may be relatively little movement of air when the substance is transported only by molecular diffusion through more stagnant portions of the layer. (Transport across the boundary layer also depends on turbulence in the air in the boundary layer. The thickness of this layer, and the air velocity and turbulence within this layer, will depend on air velocity, surface geometry and distance from the surface.) Farther away from the surface there is more air movement, which can carry the vapor away more rapidly than molecular diffusion [8].

The rate of air flow can influence volatilization both directly, as discussed above, and indirectly [6]. If the relative humidity of the air is not 100%, an increase in air speed will hasten drying of the soil. This will reduce the soil water content and thereby ultimately reduce the volatilization of the chemical. Volatilization, originally rapid, will slowly decrease until the surface concentrations of water and/or compound are depleted. The rate will eventually become constant, and the loss of the compound will become a function of the movement of compound or moisture from deeper levels. The subsequent loss of chemicals for which water can compete for adsorption sites will be related to the time it takes to dry the soil sufficiently to reduce the vapor density to an insignificantly low value [19]. The soil water content at which vapor density begins to decrease will depend upon the soil and the sorption competition with water: the more strongly adsorbed the compound is, the higher the water content at which an appreciable decrease in vapor density will occur [19].

Diffusion. When little water is being lost due to evaporation, transport of the chemical through the soil occurs by diffusion, which then becomes the rate-controlling process. Diffusion can occur in vapor and nonvapor phases. In moist soils, chemicals evidently vaporize from the water-air interface, and the concentrations at the interface are maintained by diffusion of the compound through the soil water from its adsorption sites [17]. Diffusion through the soil or soil water is a slow process, however; the chemical on the surface will evaporate relatively quickly, but that which remains in the soil will have a long lifetime.

Liquid-phase diffusion is much slower than gaseous diffusion, proceeding at a rate of only a few centimeters per month, and is associated with a much smaller scale of movement in the soil [7]. The overall diffusion rate, as well as the proportion of the total diffusion in the vapor phase, is dependent on soil water content and other factors that influence the partitioning [16]. If the soil is dry and volatilization is then related to the moisture content at the surface, the loss rate would still be controlled by diffusion, but at a much slower rate, due to lowered vapor density and hence a lowered diffusion rate in the soil.

Diffusion can occur along four major pathways, one in the vapor phase and three in nonvapor phases: air-water interface, water-water pathway, and water-solid interface. The relative amount of diffusion via each pathway depends on temperature, bulk density, and other variables that affect the partitioning between air, water, and soil [15]. Only small quantities are in the vapor phase compared with the amount in solution or adsorbed on the soil. However, as coefficients of diffusion in air are several thousand times greater than those for water or surface diffusion, total mass transport by diffusion through the vapor phase can be approximately equal to that through nonvapor phases.

Since the vapor phase diffusion coefficient is approximately 10^4 larger than the solution phase diffusion coefficient, a partition coefficient for the distribution of a chemical between the soil water and the soil air of 10^4 (g/cm^3 in soil water \div g/cm^3 in soil air) may be considered as a transition for determining when vapor or nonvapor phase diffusion becomes dominant. Chemicals with partition coefficients much smaller than 10^4 will diffuse mainly in the vapor phase, and those with partition coefficients much greater than 10^4 will diffuse primarily in the solution phase (Ref. 3 and Ref. 4 as cited in Ref. 11).

Ehlers *et al.* [1] show that vapor-phase diffusion is inversely proportional to ambient pressure, whereas nonvapor-phase diffusion is not. They give the following relationship:

$$D = D_s + D'_v (P_o/P) \quad (16-1)$$

where²

- D = actual diffusion coefficient in soil (L^2/T)
- D_s = nonvapor-phase diffusion coefficient (L^2/T)
- D'_v = apparent vapor-phase diffusion coefficient (L^2/T)
- P_o = reference pressure (standard atmospheric)
- P = ambient pressure

In practice, P will probably not deviate significantly from P_o , so that $P_o/P \approx 1$.

The influence of vapor-phase diffusion becomes less important (the apparent vapor-phase diffusion coefficient decreases) as bulk density increases and air-filled porosity decreases, leaving fewer pathways by which vapor can diffuse. The apparent vapor-phase diffusion coefficient can be expressed as

$$D'_v = (D_v s^{10/3} / \rho_b s_t^2) \frac{d\rho}{dc} \quad (16-2)$$

where

- D_v = vapor-phase diffusion coefficient in air (L^2/T)
- s = air-filled porosity
- ρ_b = bulk density (M/L^3)
- s_t = total porosity (air + water)
- ρ = vapor density (M/L^3)
- c = concentration in soil (M/L^3)

D'_v will increase with increasing $d\rho/dc$ (the change of vapor density with concentration), but above a certain critical concentration the vapor density becomes a constant and nonvapor movement controls the rate of diffusion. It has been shown for lindane [2] that the apparent nonvapor-phase diffusion coefficient increases as soil bulk density increases; therefore, if an increase in soil bulk density (and a corresponding decrease in air-filled porosity) decreases vapor movement and reduces volatility, there will be a counteracting increase in nonvapor movement.

Another equation is given by Farmer *et al.* [3]. Based on an analysis in Ref. 13, an expression for the diffusion coefficient was derived that

2. Dimensions for parameters are identified as follows: L = length, T = time, M = mass, K = temperature in degrees Kelvin.

included soil porosity terms to account for the geometric effects of the soil on the apparent steady-state diffusion:

$$D'_v = D_v (s^{10/3} / s_t^2) \quad (16-3)$$

This equation is similar to Eq. 16-2 except that it omits bulk density and vapor density correction factors.

According to Hamaker [7], vapor-phase diffusion coefficients at different temperatures and pressures may be compared as

$$D_1/D_2 = P_2/P_1 (T_1/T_2)^m \quad (16-4)$$

where P = ambient total pressure (consistent units) and T = temperature (K); m is theoretically 1.5 and is measured as 1.75-2.0.

Diffusion coefficients of different chemicals can be related by their molecular weights:

$$D_1/D_2 = \sqrt{M_2/M_1} \quad (16-5)$$

When volatilization becomes a diffusion-controlled process, diffusion equations can be used to predict both concentrations in the soil and loss rates from the soil surface by volatilization if diffusion coefficients in the soil are known [19]. (Diffusion coefficients can also be estimated by methods given in Chapter 17.)

Mass Transport by the Wick Effect. Chemicals in the soil can volatilize through the action of a process called the wick effect or wick evaporation. The chemical is transported from the soil body to the surface by capillary action. Its rate of evaporation is enhanced by the evaporation of the water causing the capillary action. Hartley [8] discusses this transport mechanism in detail. The soil column acts as a wick; the water in the soil moves up the capillaries of the wick to replenish that lost at the top by evaporation. The diffusive escape in the vapor phase causes an actual mass flow in the wick. If the liquid contains a low concentration of a solute less volatile than water, the solute will increase in concentration near the evaporating surface and cannot diffuse back down the wick as quickly as it accumulates, since diffusion in the liquid phase competes poorly with this mass flow.

Hartley states that one or more of the following can result from this process:

- The solute can become so concentrated at the surface that water evaporation is greatly reduced;
- The concentration of the solute at the surface may increase until its rate of evaporation balances its rate of arrival; and/or
- The solute may form a saturated solution in the soil water, leading to an efflorescence of crystals or powder, such as that seen on the surface of a fertile soil after drying.

The second phenomenon noted above can greatly increase the evaporation of a moderately volatile, moderately water-soluble compound. The compound will tend to be carried along with the water in the ratio present in the undisturbed soil water, not because of any peculiarity in the evaporation process (such as codistillation), but because the bulk flow of the solution up the capillaries is too fast for diffusion in the soil water to compete. The evaporation rate from the surface will remain approximately constant and rapid as long as water continues to flow up and keep the surface moist. It is only during this period of rapid water loss that evaporation of water indirectly accelerates that of the chemical. The amount of chemical volatilized is related to the time needed to dry the soil sufficiently to reduce the vapor density of the chemical [19].

16-3 METHODS FOR ESTIMATING VOLATILIZATION OF CHEMICALS FROM SOIL

A comprehensive model of the volatilization process would have to consider not only all the factors mentioned above but also soil type, ground cover, terrain, weather, soil pH, organic matter content, type of input, method of incorporation into the soil, and other factors. The magnitude and complexity of these considerations indicate the shortcomings that can be expected in theoretical studies of soil volatilization. The approximations currently available do not explicitly address the complexities of the volatilization process. The methods therefore appear to have deficiencies, although their originators point out their usefulness when applied to the particular situations and chemicals for which they were developed.

Hartley Method. Hartley [8] presents two fairly simple equations to estimate the volatilization of chemicals from soil. The method is based on an analysis of the heat balance between the evaporating chemical (or water) and air. The flux (quantity volatilizing from soil to air) is expressed as

$$f = \frac{\rho_{\max} (1-h)}{\delta} \bigg/ \left[\frac{1}{D_v} + \frac{\lambda_v^2 \rho_{\max} M}{kR T^2} \right] \quad (16-6)$$

where

- f = flux of compound (M/L^2T)
- ρ_{\max} = saturated vapor concentration at the temperature of the outer air (M/L^3)
- h = humidity of the outer air ($0 \leq h \leq 1$)
- δ = thickness of stagnant layer through which the chemical must pass (L)
- D_v = diffusion coefficient of vapor in the air (L^2/T)
- λ_v = latent heat of vaporization (cal/M)
- M = molecular weight (M/mol)
- k = thermal conductivity of air (cal/LK)
- R = gas constant (cal/mol)
- T = temperature (K)

The second term in the denominator is a thermal component of the resistance to volatilization. It is significant primarily for water or quite volatile compounds; for less volatile compounds, this term can be ignored, resulting in the following simplified form:

$$f = \frac{D_v \rho_{\max} (1-h)}{\delta} \quad (16-7)$$

Hamaker Method. Hamaker [7] proposed a method for estimating the volatilization rate of chemicals from soil. The impregnated soil layer is assumed to be semi-infinite; i.e., the total depth is large in comparison with the depth to which the soil is significantly depleted of the chemical by diffusion and volatilization. The loss of chemical is expressed as

$$Q_t = 2c_o \sqrt{Dt/\pi} \quad (16-8)$$

where

- Q_t = total loss of chemical per unit area over some time t (M/L^2)
- c_o = initial concentration of chemical in soil (M/L^3)
- D = diffusion coefficient of vapor through the soil (L^2/T)
- π = 3.14159 . . .

This equation may give low values, since it ignores mass transfer due to the wick effect.

Hamaker presented a second method based on total water loss — i.e., the loss due to vapor diffusion as well as the mass transfer of soil solution. The approximation for the loss of a dissolved, volatile chemical is

$$Q_t = \frac{P_{vp}}{P_{H_2O}} \frac{D_v}{D_{H_2O}} (f_w)_v + c (f_w)_L \quad (16-9)$$

where

f_w	= loss of water per unit area (M/L^2)
P_{vp}	= vapor pressure of chemical
P_{H_2O}	= vapor pressure of water
D_v	= diffusion coefficient of chemical in air (L^2/T)
D_{H_2O}	= diffusion coefficient of water vapor in air (L^2/T)
sub V	= loss of vapor
sub L	= loss of liquid
c	= concentration of chemical in soil solution (M/M)

The use of this equation requires knowledge of the water flow in the soil as well as diffusion coefficients for water vapor and the chemical in question.

Mayer, Letey, and Farmer Method. Mayer *et al.* [12] applied the diffusion laws to the mathematical description of the movement of chemicals in soils under a concentration gradient. Diffusion is assumed to be the only mechanism supplying chemicals to the soil surface; therefore, the approach probably underestimates the volatilization rate. An analogy is drawn between the heat transfer equation (Fourier's law) and the transfer of matter under a concentration gradient (Fick's law). The equation is solved for various boundary conditions.

The one-dimensional diffusion equation, with a constant diffusion coefficient, D , is

$$\frac{\partial^2 c}{\partial z^2} - \frac{1}{D} \frac{\partial c}{\partial t} = 0 \quad (16-10)$$

where

c	= concentration in the soil (M/L^3)
z	= distance measured normal to the soil surface (down is positive, surface is zero) (L)

D = diffusion coefficient in soil (L^2/T)

t = time (T)

Five different solutions are presented, each applicable to a different set of boundary conditions. The models and their basic assumptions are described below. In addition to those defined above, the following variables are used:

L = soil layer depth (L)

v = air flow velocity (L/T)

c_a = concentration in air (M/L^3)

R_o = isotherm coefficient, ratio of concentration in air to concentration in soil. (In moist soils this ratio might be approximated by the ratio of Henry's Law constant to the soil adsorption coefficient.)

• *Model I.* In this model it is assumed that the compound volatilizes and is removed rapidly from the soil surface, maintaining a zero concentration at the surface. The flux at any time in the model depends only on the diffusion coefficient, which must remain constant over the time period of interest. No diffusion occurs across the lower boundary. It would be difficult to predict volatilization rates in the field using this model, because the boundary conditions would not necessarily conform to those in the model or supporting experiments. However, the assumed zero concentration at the surface would be approached even if wind speeds were only about 2 cm/s.

The boundary conditions are:

$$\left. \begin{aligned} c &= c_o \text{ at } t = 0 \quad 0 \leq z \leq L \\ c &= 0 \text{ at } z = 0, t > 0 \\ \frac{\partial c}{\partial z} &= 0 \text{ at } z = L \end{aligned} \right\} \quad (16-11)$$

The solution of the diffusion equation with these boundary conditions is³

$$c(z,t) = \frac{4c_o}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} e^{-D(2n+1)^2 \pi^2 t/4L^2} \cos \frac{(2n+1)\pi(L-z)}{2L} \quad (16-12)$$

3. Eqs. 16-12, -13, -22, -24, -26, -29 and -31 all contain either a $\sum_{n=0}^{\infty}(\dots)$ or a $\sum_{n=1}^{\infty}(\dots)$. In practice the summation can be terminated after the terms converge for the second or third significant figure, and this will almost always be less than ten terms (i.e., $n \leq 10$). In some cases convergence at $n = 2$ will be found.

and the flux is given by

$$f = \frac{Dc_0}{\sqrt{\pi Dt}} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-n^2 L^2 / Dt} \right] \quad (16-13)$$

• *Model II.* If the value of the summation term in Eq. 16-13 is negligible in comparison to 1, the equation can be simplified. The summation will be small if the expression in the exponential, $n^2 L^2 / Dt$, is large, say on the order of 10 or more. This simplified model is applicable until the concentration at the lower boundary drops by 1%, i.e. until time $t = L^2 / 14.4 D$.

As in model I, this model may not predict actual volatilization rates in the field, where the boundary conditions may not prevail.

With increasing L and decreasing D or t (which increases the value of the term in the exponential of Eq. 16-13), the flux becomes

$$f = \frac{Dc_0}{\sqrt{\pi Dt}} = c_0 \sqrt{D/\pi t} \quad (16-14)$$

The total quantity volatilized equals the product of flux and time, giving total loss per unit area, $Q = c_0 \sqrt{Dt/\pi}$. As noted in Eq. 16-8, the value of Q derived by Hamaker [7] is twice as large. The reason for this discrepancy is not clear.

The concentration in the soil column for the same boundary conditions as in Model I can be expressed as

$$c(z,t) = c_0 \operatorname{erf} \left(\frac{z}{2\sqrt{Dt}} \right) \quad (16-15)$$

where "erf" is the error function, which may be evaluated by the methods described in §16-5. These equations are valid until time $t = L^2 / 14.4D$.

• *Model III.* This model is similar to Model I, except that it allows for diffusion downward across a boundary at $z = L$.

The boundary conditions are

$$\left. \begin{aligned} c &= c_0 \text{ at } t = 0, 0 \leq z \leq L \\ c &= 0 \text{ at } t = 0, z > L \\ c &= 0 \text{ at } t > 0, z = 0 \end{aligned} \right\} \quad (16-16)$$

The concentration in the soil column is

$$c(z,t) = \frac{c_0}{2} \left[2 \operatorname{erf} \left(\frac{z}{2\sqrt{Dt}} \right) - \operatorname{erf} \left(\frac{z-L}{2\sqrt{Dt}} \right) - \operatorname{erf} \left(\frac{z+L}{2\sqrt{Dt}} \right) \right] \quad (16-17)$$

The flux is

$$f = D \frac{\partial c}{\partial z} \bigg|_{z=0} \quad (16-18)$$

so that

$$f = \frac{Dc_0}{\sqrt{\pi Dt}} (1 - e^{-L^2/4Dt}) \quad (16-19)$$

For large values of $L^2/4Dt$, less than 1% error will result in using

$$f = \frac{Dc_0}{\sqrt{\pi Dt}} \quad (16-20)$$

if $e^{-L^2/4Dt} < 0.01$ or $t < L^2/18.4 D$.

- *Model IV.* This model accounts for a concentration that varies with time at the soil surface instead of being always zero. The rate at which the chemical is removed by the air is then a limiting factor in the volatilization rate. The chemical is uniformly distributed to depth L , and there is no flux through the lower boundary. A continuous flow of fresh air at velocity v passes over the soil surface, so background concentration is low. The concentration in the air, c_a , after removal is uniform at a constant fraction of the concentration at the soil surface. This implies rapid mixing in the air, due either to turbulence or a large air diffusion coefficient. The model does not include diffusion in the transfer process, only convective mass transfer: if the air stops moving, the flux of chemical into the air becomes zero. Thus, the model is appropriate if the convective flow due to air movement is considerably greater than the flow due to a diffusion process. Again, this model may not accurately predict volatilization rates in the field, where the boundary conditions may not prevail.

The boundary conditions are:

$$\left. \begin{aligned} c &= c_0 \text{ at } t = 0, 0 \leq z \leq L \\ \frac{\partial c}{\partial z} &= 0 \text{ at } z = L \\ f &= v c_a \text{ at } t > 0, z = 0 \end{aligned} \right\} \quad (16-21)$$

The concentration in the soil is

$$c(z,t) = 2c_0 \sum_{n=1}^{\infty} \left\{ \frac{e^{-D\alpha_n^2 t} (h - R_0 \alpha_n^2) \cos [\alpha_n (L-z)]}{[L(h - R_0 \alpha_n^2)^2 + \alpha_n^2 (L + R_0) + h] \cos \alpha_n L} \right\} \quad (16-22)$$

where $h = R_0 v/D$ and α_n are the roots of

$$\alpha_n \tan (\alpha_n L) = \frac{R_0 v}{D} - R_0 \alpha_n^2 \quad (16-23)$$

R_0 is an adsorption isotherm coefficient which relates concentration in air, c_a , over a solid onto which the compound is adsorbed to the concentration of the compound on the solid, c_s .

For most cases, $R_0 \alpha_n^2 \ll R_0 v/D$, so Eq. 16-22 can be simplified to

$$c(z,t) = 2c_0 \sum_{n=1}^{\infty} \left\{ \frac{e^{-D\alpha_n^2 t} (R_0 v/D) \cos [\alpha_n (L-z)]}{[L (R_0 v/D)^2 + \alpha_n^2 L + (R_0 v/D)] \cos \alpha_n L} \right\} \quad (16-24)$$

where α_n are the roots of

$$\alpha_n \tan (\alpha_n L) = \frac{R_0 v}{D} \quad (16-25)$$

Flux through the surface is

$$f = 2 D c_0 \sum_{n=1}^{\infty} \left[\frac{(R_0 v/D)^2 e^{-D\alpha_n^2 t}}{L (R_0 v/D)^2 + \alpha_n^2 L + (R_0 v/D)} \right] \quad (16-26)$$

The concentration in the air (c_a) is simply R_0 times the estimated concentration in the soil (c_s) at the surface, for the range of concentrations over which R_0 is valid.

• **Model V.** In this model, chemical at the surface diffuses into a stationary air layer. The diffusion coefficient of the chemical in the air is D_v and the thickness of the air layer is d . The concentration in the air at the soil surface is $R_o c$ (where c is concentration at the soil surface, c_s), so the flux from the soil is

$$f = D_v R_o c / d \quad (16-27)$$

Initial and boundary conditions are

$$\left. \begin{aligned} c &= c_o \text{ at } t = 0, 0 \leq z \leq L \\ \frac{\partial c}{\partial z} &= 0 \text{ at } z = L \\ f &= (D_v R_o c_s) / d \text{ at } t > 0, x = 0 \\ c &= c_s \text{ at } t > 0, z = 0 \end{aligned} \right\} \quad (16-28)$$

The concentration in the soil is

$$c(z,t) = \frac{2D_v R_o c_o}{Dd} \sum_{n=1}^{\infty} \left\{ \frac{e^{-D\alpha_n^2 t} \cos[\alpha_n(L-z)]}{[L(D_v R_o / Dd)^2 + L\alpha_n^2 + D_v R_o / Dd] \cos \alpha_n L} \right\} \quad (16-29)$$

where α_n are the roots of

$$\alpha_n \tan(\alpha_n L) = \frac{D_v R_o}{Dd} \quad (16-30)$$

The flux at the surface is

$$f = 2Dc_o \sum_{n=1}^{\infty} \left[\frac{e^{-D\alpha_n^2 t} (D_v R_o / Dd)^2}{L(D_v R_o / Dd)^2 + L\alpha_n^2 + D_v R_o / Dd} \right] \quad (16-31)$$

• **Choosing the Appropriate Model.** Models I, II, and III appear to be valid when compared with the results of laboratory experiments, but predictions for field conditions would be subject to error because the boundary and environmental conditions such as wind velocity, incorporation depth, and water movement are not as well defined as they

are in the laboratory. The models should make reasonable estimates of losses by diffusion, however.

For a chemical incorporated in a soil surface layer, if diffusion is the only transfer mechanism to the surface, use:

Models I, If wind velocity is greater than about 2 cm/s.
 II or III

Model IV If air is moving over the soil but is already enriched with chemical, due possibly to movement over contaminated soil upwind.

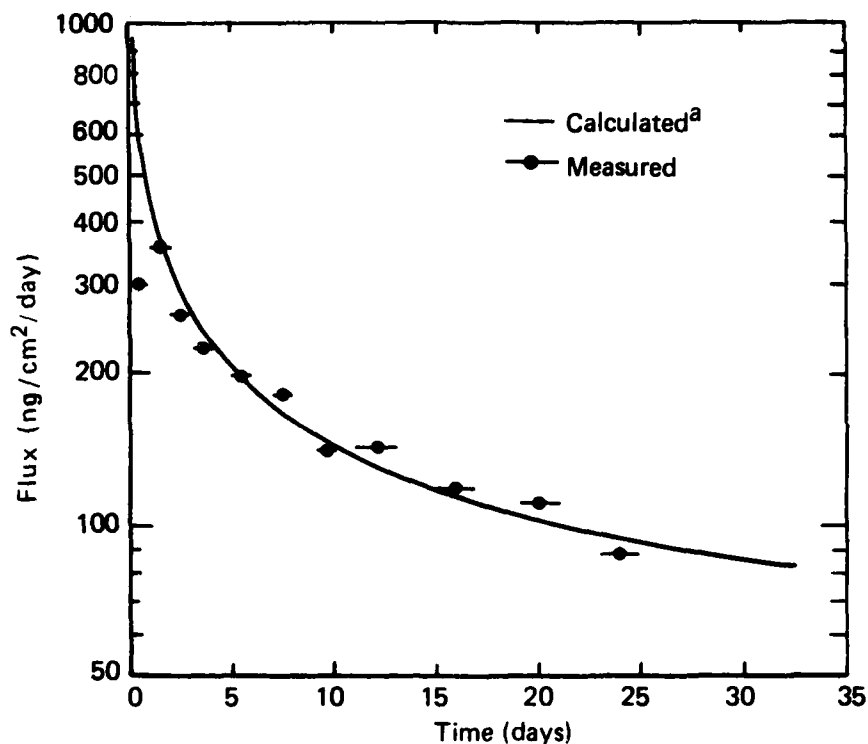
Model V If a stationary air layer is in contact with the surface, such as when the air movement is restricted by a standing crop.

Mayer *et al.* [12] compared results from published laboratory experiments on the volatilization of dieldrin and lindane with predictions from these models. Figure 16-2 shows a comparison with model II. The conditions of the experiments were compatible with the requirements of the model; i.e., airflow over the surface maintained zero concentration at the air/soil interface, and the depth of the soil column could be assumed infinite for several hundred days. The model appears to offer good predictions under these conditions.

Figure 16-3 compares the results of models I, II and IV with data from a lindane volatilization experiment. Under the conditions of the experiment, the concentration at the lower boundary decreased by one percent quite rapidly, which accounts for the difference between the results of models I and II. Model IV predictions are better, because the air velocity across the experimental setup was not sufficient to maintain a zero concentration at the interface.

Figure 16-4 compares models II and IV with experimental data and illustrates the importance of choosing an appropriate model when airflow velocity affects chemical concentrations at the surface. Model II, which does not take air velocity (v) into account, is reasonably accurate at higher velocities. The model IV equations, however, contain v and adjust the calculated flux to reflect non-zero surface concentrations caused by low-velocity airflow.

Jury, Grover, Spencer, and Farmer Method. Jury *et al.* [10] have presented another method for predicting the flux of a chemical in both



a. Diffusion coefficient assumed to be $2.3 \text{ mm}^2/\text{week}$.

Source: Mayer *et al.* [12]

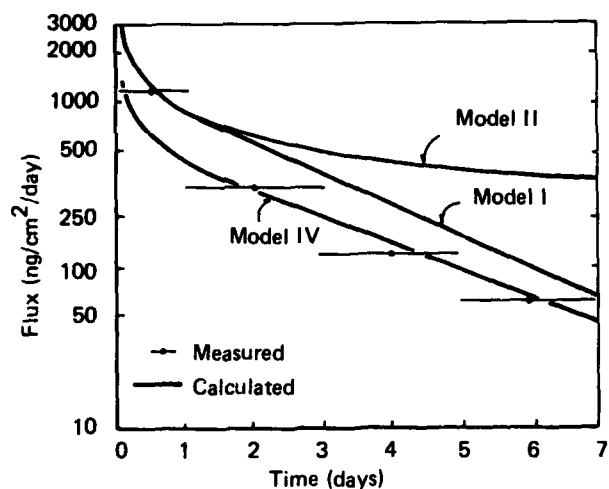
FIGURE 16-2 Dieldrin Flux: Comparison of Measured Values with Those Calculated by Model II

the presence and absence of the wick effect. In their work with the pesticide triallate, they expressed the total concentration of a chemical in the soil as:

$$c_t = \rho_b c_s + \theta c_l + \eta c_g \quad (16-32)$$

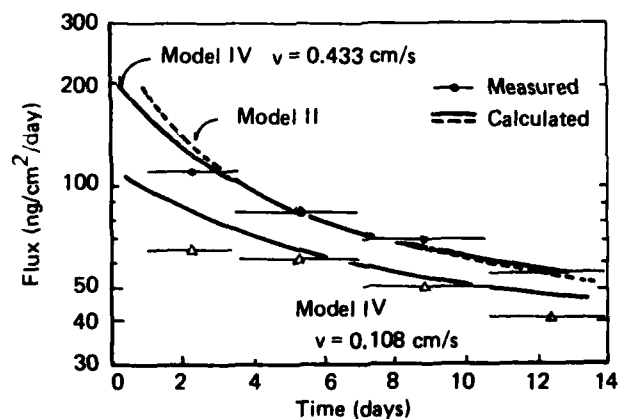
where

- c_t = total concentration in soil (M/L^3 soil)
- ρ_b = soil bulk density (M/L^3)
- c_s = adsorbed concentration (M/M)
- θ = volumetric soil water content (L^3/L^3)
- η = soil air content (L^3/L^3)
- c = concentration in the liquid phase (M/L^3 water)
- c_g = concentration in the gas phase (M/L^3 air)



Source: Mayer *et al.* [12]

FIGURE 16-3 Lindane Flux from Treated Gila Silt Loam: Comparison of Measured and Calculated Values



v = Velocity of air over soil surface

Source: Mayer *et al.* [12]

FIGURE 16-4 Dieldrin Volatilization Flux from Uniformly Treated Gila Silt Loam at Two Air Velocities: Comparison of Measured and Calculated Values

The flux is:

$$f = -D_g \frac{\partial c_g}{\partial z} - D_l \frac{\partial c_l}{\partial z} - f_w c_l \quad (16-33)$$

where

$$\begin{aligned} f &= \text{chemical flux (M/L}^2 \cdot \text{T)} \\ D_g &= \text{gas diffusion coefficient (L}^2/\text{T)} \\ D_l &= \text{liquid diffusion coefficient (L}^2/\text{T)} \\ f_w &= \text{water flux (L}^3/\text{L}^2 \cdot \text{T)} \end{aligned}$$

The transport terms in the gas phase, $D_g(\partial c_g/\partial z)$, in the liquid phase, $D_l(\partial c_l/\partial z)$, and along with the soil water, $f_w c_l$, can be seen. The continuity equation is:

$$\frac{\partial c_t}{\partial t} + \frac{\partial f}{\partial z} = 0 \quad (16-34)$$

These three equations can be solved to give concentrations in the soil column, along with the flux and total amount lost. The following assumptions have been made:

- (1) c_l and c_g are related by Henry's Law, with $K_H = c_l/c_g$. (K_H will have units of $L^3 \text{ air}/L^3 \text{ water}$. Note that K_H is the inverse of the usual Henry's Law constant (H) used in other chapters.)
- (2) Adsorption isotherms are linearized over the range of concentrations so that $c_s = \alpha c_l + \beta$ (where α and β are parameters of the adsorption isotherm);
- (3) Diffusion coefficients D_g and D_l are constant (i.e., the soil is homogeneous);
- (4) The water flux, f_w , is either zero or equal to a constant evaporation rate;
- (5) The gas concentration c_g above the soil remains zero, indicating that the air carries the pollutant away rapidly; and
- (6) The soil column is infinitely deep.

Assumptions (1) and (2) permit the elimination of c_s and c_l from Eq. 16-32:

$$\begin{aligned} c_t &= \rho_b [\alpha (K_H c_g) + \beta] + \theta (K_H c_g) + \eta c_g \\ &= (\rho_b K_H \alpha + \theta K_H + \eta) c_g + \beta \rho_b \end{aligned} \quad (16-35)$$

$$c_t = \epsilon c_g + \gamma \quad (16-36)$$

Similarly, through assumptions (1) and (3), Eq. 16-33 can be written as:

$$\begin{aligned} f &= -D_g \frac{\partial c_g}{\partial z} - D_l K_H \frac{\partial c_g}{\partial z} - f_w (K_H c_g) \\ &= -(D_g + K_H D_l) \frac{\partial c_g}{\partial z} - K_H f_w c_g \end{aligned} \quad (16-37)$$

or

$$f = -D_e \frac{\partial c_g}{\partial z} - V_e c_g \quad (16-38)$$

where

$$\begin{aligned} D_e &= \text{effective diffusion coefficient } (D_g + K_H D_l) \\ V_e &= \text{effective convection velocity } (K_H f_w) \end{aligned}$$

As expressed by Eq. 16-38, all transport is combined into the gas phase.

The continuity equation (16-34) can be expressed solely in terms of the gas-phase concentration by the substitution of Eqs. 16-36 and -38:

$$\begin{aligned} \frac{\partial}{\partial t} (\epsilon c_g + \gamma) &= - \frac{\partial}{\partial z} (-D_e \frac{\partial c_g}{\partial z} - V_e c_g) \\ \epsilon \frac{\partial c_g}{\partial t} &= D_e \frac{\partial^2 c_g}{\partial z^2} + V_e \frac{\partial c_g}{\partial z} \end{aligned} \quad (16-39)$$

This reduces the number of parameters necessary to apply the equations. The boundary conditions are expressed as follows:

$$\left. \begin{aligned} c_g &= 0 \text{ at } z = 0, t \geq 0 \\ c_g &= (c_{t_0} - \gamma)/\epsilon \text{ at } t = 0, z \geq 0 \\ c_g &= (c_{t_0} - \gamma)/\epsilon \text{ at } t = 0, z = \infty \end{aligned} \right\} \quad (16-40)$$

These solutions to Eq. 16-40 are the concentrations as a function of depth and time:

For $f_w = 0$,

$$c_g(z,t) = \frac{c_{t_0} - \gamma}{\epsilon} \operatorname{erf} \left(\frac{z}{2} \sqrt{D_e t / \epsilon} \right) \quad (16-41)$$

For $f_w \neq 0$,

$$c_g(z,t) = \left(\frac{c_{t_0} - \gamma}{\epsilon} \right) \left[1 - \frac{1}{2} \operatorname{erfc} \left(\frac{z + (V_e t / \epsilon)}{2 \sqrt{D_e t / \epsilon}} \right) - \frac{1}{2} e^{-V_e z / D_e} \operatorname{erfc} \left(\frac{z - (V_e t / \epsilon)}{2 \sqrt{D_e t / \epsilon}} \right) \right] \quad (16-42)$$

where:

$$\operatorname{erfc}(x) = 1 - \operatorname{erf}(x) \quad (16-43)$$

The flux at the surface for any time t , $f(0,t)$, for the two cases of soil water flux $= 0$ and $\neq 0$ is:

For $f_w = 0$,

$$f(0,t) = -(c_{t_0} - \gamma) \sqrt{D_e / \epsilon \pi t} \quad (16-44)$$

For $f_w \neq 0$,

$$f(0,t) = -(c_{t_0} - \gamma) \sqrt{D_e / \epsilon \pi t} e^{-w^2} - V_e \left(\frac{c_{t_0} - \gamma}{2\epsilon} \right) [1 + \operatorname{erf}(w)] \quad (16-45)$$

where

$$w^2 = V_e^2 t / 4 D_e \quad (16-46)$$

The total chemical loss when $f_w = 0$ can be found by integrating Eq. 16-44, which yields the following:

$$Q_t(t) = 2(c_{t_0} - \gamma) \sqrt{D_e t / \epsilon \pi} \quad (16-47)$$

Error may result from these models because of the behavior of the diffusion coefficient. As soil becomes more saturated with water, the pore space is decreased. This, in turn, reduces the diffusion coefficient proportionally to soil air space, η , at high air content until intermediate satura-

tion is reached and then proportionally to some higher power of η . The use of a measured effective diffusion coefficient corresponding to the conditions of interest would lessen the potential for error. Some discrepancy may also be introduced by the use of linear adsorption isotherms; the adsorption isotherm may be curvilinear, with larger differences occurring at low concentrations.

In laboratory experiments with triallate and two soils, Jury *et al.* found reasonable agreement between the models and measured data. They noted a smaller discrepancy in the absence of water flux, when diffusion was the only transport mechanism. Results also indicated that flow occurred primarily by liquid convection below the surface layer. Depletion of the pesticide was high only in the top 1 centimeter or so of the soil column; 90% of the pesticide remained after about a month. Surface depletion caused a rapid decrease in volatilization with time, and rate of movement to the soil surface became the controlling factor in chemical loss. Most of the compound was sorbed and not free to move. The experiments indicated the relative importance of convective mass flow, diffusive transport, and soil properties. In the two soils used, a higher adsorptive capacity was partially mitigated by a lower bulk density, resulting in a higher diffusion coefficient. The two soils, though different in these respects, showed similar losses under diffusion-controlled volatilization.

These models generally predict the upper limit of the volatilization rate.

Dow Method. Scientists at Dow Chemical Company have conducted experiments to establish the relationships between vapor pressure, water solubility, and soil adsorption coefficient as they relate to the volatility from the soil of a chemical applied to the soil surface [20]. They studied nine chemicals (Table 16-1) and derived a correlation that could predict the volatilization of these chemicals from a soil surface under laboratory conditions. The volatilization rate was found to be proportional to the factor P_{vp}/SK_{oc} where P_{vp} is vapor pressure in mm Hg, S is water solubility in mg/L or ppm, and K_{oc} is the soil adsorption coefficient in $(\mu\text{g/g})/(\mu\text{g/mL})$. Half-life for depletion of the chemical from the surface was found to be:

$$t_{1/2} = 1.58 \times 10^{-8} \left(\frac{K_{oc} S}{P_{vp}} \right) \text{ days} \quad (16-48)$$

TABLE 16-1
Chemical Properties and Volatilization Rate Constants for
Chemicals Applied to the Soil Surface

Chemical	Vapor Pressure, P_{vp} (mm Hg)	Water Solubility (ppm)	Soil Adsorption Constant, K_{oc}	$\frac{P_{vp}}{S K_{oc}}$	Initial Rate Constant (hr^{-1})	Predicted Rate Constant (hr^{-1}) Eq. 16-49
Nitrapyrin	3×10^{-3}	4	600	1.2×10^{-6}	6.4×10^{-1}	2.2
Lindane	8×10^{-5}	7	2,500	7.9×10^{-9}	4.4×10^{-2}	1.4×10^{-2}
Trifluralin	1.3×10^{-4}	0.6	6,000	3.6×10^{-8}	2.6×10^{-2}	6.6×10^{-2}
Chlorpyrifos	1.9×10^{-5}	2	13,000	7.3×10^{-10}	8.8×10^{-2}	1.3×10^{-3}
Diuron	1.9×10^{-6}	42	150	2.9×10^{-10}	2.5×10^{-3}	5.3×10^{-4}
Carbofuran	2.0×10^{-6}	415	10	1.6×10^{-10}	1.2×10^{-3}	2.9×10^{-4}
Dinoseb	5×10^{-5}	50	700	1.4×10^{-9}	1.1×10^{-3}	2.6×10^{-3}
DDT	2.7×10^{-7}	0.0012	240,000	6.8×10^{-10}	6.9×10^{-4}	1.2×10^{-3}
Atrazine	8.5×10^{-7}	24	150	2.3×10^{-10}	6.4×10^{-4}	4.2×10^{-4}

Source: Swann *et al.* [20]

and the rate constant for volatilization is:

$$k_v = \frac{0.693}{t_{1/2}} \text{ day}^{-1} = 4.4 \times 10^7 \left(\frac{P_{vp}}{K_{oc} S} \right) \text{ day}^{-1} \quad (16-49)$$

The agreement between measured and predicted half-lives appears to be good (Table 16-2). Predictions by the method shown above were compared with measured rates of four pesticides volatilizing from a field. The chemicals and the comparisons are shown in Table 16-3; the agreement between laboratory data based estimates and field measurements appears to be within a factor of four. The effect of environmental properties such as soil moisture, soil type, temperature, and wind conditions are not incorporated in this simple model.

16-4 SELECTION OF METHOD

The methods discussed in §16-3 can be used to estimate the quantity of chemical that volatilizes from the soil. Not all methods are applicable to a given situation. This section describes how the proper method is selected and used. Table 16-4 summarizes the characteristics of the methods, and Figure 16-5 is a decision chart that outlines the model selection process. Refer to this chart when following the procedure given below.

Basic Steps

- (1) If the chemical is not distributed throughout the soil, the Dow method, which computes the volatilization rate for a surface-applied chemical, is appropriate. Follow step (2). If the chemical is distributed throughout the soil, proceed to step (3).
- (2) The Dow method estimates the volatilization rate of a chemical applied to the surface only. The data required include solubility (S), vapor pressure (P_{vp}), and soil adsorption coefficient (K_{oc}) for the chemical. Equation 16-48 can be used to estimate the half-life of the chemical in the soil. Equation 16-49 estimates the volatilization rate constant based on the estimated half-life. The concentration of chemical on the surface at any time can be estimated from

$$c = c_0 e^{-k_v t} \quad (16-50)$$

TABLE 16-2

Comparison of Measured Volatilization Half-lives
with Values Predicted by the Dow Method

Chemical	Laboratory- Measured Volatility Half-life (days)	Predicted Volatility Half-life (days)
Nitrapyrin	0.05	0.02
Lindane	0.70	2.0
Trifluralin	1.0	0.4
Chlorpyrifos	3.0	2.2
Diuron	12	52
Carbofuran	24	33
Dinoseb	26	12
DDT	42	23
Atrazine	45	69

Source: Swann *et al.* [20]

TABLE 16-3

Comparison of Field-Measured, Laboratory-Measured,
and Predicted Half-lives Using the Dow Method

Chemical	Half-life in Field (days)	Half-life in Laboratory (days)	Predicted Half-life (days)
Lindane	3.0	0.7	2.0
Trifluralin	1.5	1.0	0.4
Chlordane	6.0	—	2.5
Heptachlor	1.5	—	0.4

Source: Swann *et al.* [20]

TABLE 16-4

Models Used to Compute Volatilization of Chemicals from Soil

Method	Equations	Calculational Difficulty	Information Required	
			Chemical	Environmental
Hartley	16-7,8	Low	<ul style="list-style-type: none"> Saturated vapor concentration Vapor diffusion coefficient in air Latent heat of vaporization Molecular weight of chemical Thermal conductivity of air Gas constant 	<ul style="list-style-type: none"> Humidity Stagnant air layer thickness Temperature
Hamaker No Water Loss	16-9	Low	<ul style="list-style-type: none"> Vapor diffusion coefficient in soil Vapor pressure of chemical Vapor pressure of water 	<ul style="list-style-type: none"> Initial concentration Water flux from plot – both liquid and vapor phase
Water Loss	16-10	Low	<ul style="list-style-type: none"> Vapor diffusion coefficient in soil – for chemical and water 	
Mayer, Letey, and Farmer (Five Models)	16-12 through 16-32	High	<ul style="list-style-type: none"> Air/soil concentration isotherm coefficient Diffusion coefficient in soil Diffusion coefficient in air 	<ul style="list-style-type: none"> Depth of soil column Air flow velocity Initial concentration Adsorbed concentration Thickness of non-moving air layer
Jury, Grover, Spencer and Farmer	16-33 through 16-48	Medium	<ul style="list-style-type: none"> Gas-phase diffusion coefficient Liquid-phase diffusion coefficient Adsorption parameters Henry's law constant 	<ul style="list-style-type: none"> Total concentration in soil Soil bulk density Adsorbed concentration Volumetric soil water content Chemical concentration in liquid phase Chemical concentration in gas phase Soil air content Water flux from plot
Dow	16-49,50	Low	<ul style="list-style-type: none"> Soil adsorption coefficient Vapor pressure Solubility 	

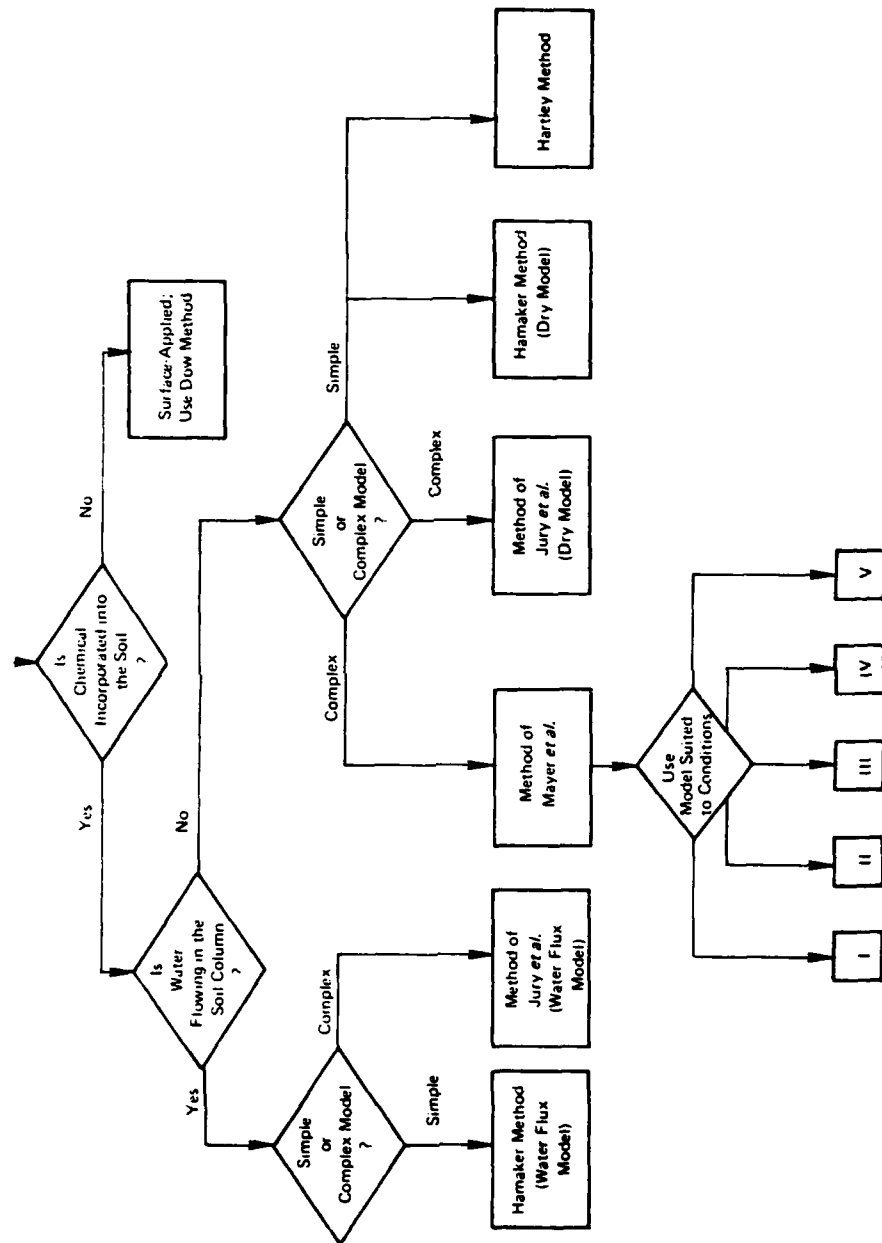


FIGURE 16-5 Decision Chart for Selecting Estimation Method

where

c_o = concentration at $t = 0$ (M/L^3)

k_v = volatilization rate constant (T^{-1})

t = time (T)

- (3) If the chemical is incorporated into the soil, the flow of water in the soil column is important. If the soil is wet and water is flowing up through the soil column to the surface and evaporating there, go to step (4). This water will be flowing due to the water concentration gradient created by the evaporation of soil water. If the soil is dry, or if no water is flowing in the soil column because of reduced evaporation at the surface, the volatilization is controlled by slow diffusion. In this case, go to step (5).
- (4) Two methods — one simple and the other complex — are presented here to estimate volatilization in the case of water flux in the soil column. It is suggested that both be used if the requisite data are available and that the estimates be compared.
 - Hamaker [7] presents a method based on total water loss from a plot of land and incorporates vapor diffusion as well as mass transfer of soil solution. Data required are the liquid and vapor flux of water per unit area of soil surface $[(f_w)_v$ and $(f_w)_L]$, the vapor pressure of the chemical and water $[P_{vp}$ and $P_{H_2O}]$, and the diffusion coefficient of the chemical and water (D and D_{H_2O}). Equation 16-9 is used to estimate the flux of the chemical.
 - Jury *et al.* [10] present a computationally more complex model to estimate the chemical flux in the presence of water flux. The equations used require values for the diffusion coefficient — either an effective coefficient (D_e) or gas-phase and liquid-phase diffusion coefficients (D_g and D_l) — soil bulk density (ρ_b), Henry's law constant for the chemical (H), adsorption isotherms (α , β parameters), soil air content (η), soil water content (θ), and soil water flux (f_w). Equation 16-42 estimates concentrations in the gas phase in the soil column as a function of time and depth. Equation 16-45 estimates flux as a function of time.
- (5) Three basic methods are available to determine volatilization in the case of no water flux: a simple one, and two

that are computationally more complex. It is suggested that values of the flux be estimated by all methods if possible and compared before they are accepted.

- *Simple Method* — Hartley proposes the use of Eq. 16-6 to predict the volatilization flux of chemicals that are highly volatile and Eq. 16-7 for those that are less volatile. These equations require the chemical saturated vapor concentration (ρ_{\max}), humidity of the air (h), the thickness of the stagnant boundary layer through which the chemical must pass (δ), and the vapor diffusion coefficient (D_v). For the more volatile compounds, one must also know the latent heat of vaporization (λ_v), molecular weight (M), thermal conductivity of air (k), and the gas constant (R).

Hamaker suggests the use of Eq. 16-8 to predict the total amount of chemical volatilized as a function of time. Required data are the diffusion coefficient in soil (D) and initial soil concentration (c_0). If the diffusion coefficients are not known, they can be estimated by Eqs. 16-1 through 16-5, as appropriate; other methods are discussed in Chapter 17.

- *More Complex Method of Jury et al.* — The method presented by Jury *et al.* [10] can be used to predict concentrations and flux. The data required for these computations are the diffusion coefficient — either an effective diffusion coefficient (D_e) or gas-phase and liquid-phase diffusion coefficients (D_g and D_l) — soil bulk density (ρ_b), Henry's law constant for the chemical (H), adsorption isotherms (α , β parameters), soil air content (η), soil water content (θ), and soil water flux (f_w). The equations applicable to the case of no water flux ($f_w=0$) are 16-41 and 16-44. Equation 16-47 estimates the total amount lost.
- *More Complex Model of Mayer et al.* — The models proposed by Mayer *et al.* [12] can be used to estimate concentrations in the soil column. Five different models, applicable to different conditions, are available. The proper one should be selected according to its applicability to the environmental conditions of interest. Although these models are computationally complex, simplifications can be introduced to make them more tractable. Some of the equations involve a series summa-

tion requiring the addition of an infinite number of terms. In practice, the summation can be terminated after the terms begin to converge for the second or third significant figure. Ten terms should show the convergence, and the series can be terminated when the last term is less than ten percent of the sum. This summation will be a reasonable approximation of the whole value.

Equations 16-25 and -30 used in models IV and V require a solution for the roots of a transcendental equation. The user may employ an iterative procedure to find the roots or a programmable calculator or computer having a program to find values of the free parameter (α_n) that solve the equation.

Model I (see Eqs. 16-11 through 16-13) is used when the concentration of a chemical remains at zero at the surface due to a wind speed greater than about 2 cm/s. No diffusion occurs across the lower boundary of the soil column. Input data required for the use of this model are initial concentration in the soil column (c_0), depth of the soil column (L), and the effective diffusion coefficient of the chemical in the soil (D). Equation 16-12 can be used to estimate concentrations $c(z,t)$ in the soil column as a function of time and depth. Equation 16-13 can be used to estimate the flux of the chemical.

Model II (see Eqs. 16-14 and -15) can be used for the same environmental conditions as model I. A simplification introduced in Eq. 16-13 in model I is also applicable to model II, as described in the text. Equation 16-14 can be used to estimate the flux. Equation 16-15 can be used to estimate concentrations in the soil column.

Model III (see Eqs. 16-16 through 16-20) is applicable under the same environmental conditions as for model I but allows for diffusion downward across the lower boundary. Equation 16-17 can be used to compute concentrations in the soil column, and Eqs. 16-19 and -20 give estimates of the flux.

Model IV (see Eqs. 16-21 through 16-26) accounts for a finite chemical concentration at the surface. The lower boundary is assumed to be impermeable. The chemical does not diffuse into the air; it is carried away only by convection. Consequently, if the air is not moving, the

model will not accurately predict the flux. This model should be used if there is a finite initial concentration of chemical in the air through depletion from the soil surface upwind. Equation 16-24 estimates the concentration in the soil column, and Eq. 16-26 estimates the flux.

Model V (see Eqs. 16-27 through 16-31) is applicable if the air in contact with the soil surface is stagnant, such as might occur if there is a standing crop on the surface. Equation 16-29 estimates the concentration in the soil column, and Eq. 16-31 estimates the flux.

In the examples that follow, concentrations and fluxes are estimated by each of the principal methods described above. To facilitate comparison of the results, all examples refer to trichloroethylene (TCE) and the conditions are as similar as possible. The chemical and environmental data used in the calculations are listed in Table 16-5.

Example 16-1 Hartley Method, No Water Flux

- (1) Since TCE is quite volatile, Eq. 16-6 is appropriate. Table 16-5 lists all the required parameters. The diffusion coefficient of the vapor in air (D_v) was estimated by Eq. 16-5. Compounds whose vapor-phase diffusion coefficients at 293K are known include carbon disulfide ($M = 76, D = 0.102$) and diethyl ether ($M = 74, D = 0.089$). Substitute the values of M and D for each of these compounds in Eq. 16-5 and average the results.

$$\text{Using carbon disulfide: } D_v/0.102 = \sqrt{76/131.5}$$

$$D_v = 0.077 \text{ cm}^2/\text{s}$$

$$\text{Using diethyl ether: } D_v/0.089 = \sqrt{74/131.5}$$

$$D_v = 0.067 \text{ cm}^2/\text{s}$$

$$\text{Average } D_v = 0.072 \text{ cm}^2/\text{s}$$

- (2) Substitute the above in Eq. 16-6 to find the flux, f .

$$f = \frac{(4.3 \times 10^{-4} \text{ g/cm}^3)(0.5)}{0.3 \text{ cm}} \\ = \frac{1}{0.072 \text{ cm}^2/\text{s}} + \frac{(63.2 \text{ cal/g})^2 (4.3 \times 10^{-4} \text{ g/cm}^3)(131.5 \text{ g/mol})}{(61 \times 10^{-6} \text{ cal/s} \cdot \text{cm} \cdot \text{K})(1.987 \text{ cal/mol} \cdot \text{K})(293\text{K})^2} \\ = 5.04 \times 10^{-5} \text{ g/cm}^2 \cdot \text{s}$$

TABLE 16-5

Chemical and Environmental Data for
Estimation of Trichloroethylene Volatilization^a

Parameter	Symbol	Value
Characteristics of TCE at T = 293K		
Saturated vapor concentration	ρ_{\max}	$4.3 \times 10^{-4} \text{ g/cm}^3$
Diffusion coefficient in air	D_v	$0.072 \text{ cm}^2/\text{s}$ (see Example 16-1)
Heat of vaporization	λ_v	63.2 cal/g
Thermal conductivity of air	k	$61 \times 10^{-6} \text{ cal/s-cm-K}$
Gas constant	R	1.987 cal/mole-K
Diffusion coefficient of vapor through soil	D	$0.039 \text{ cm}^2/\text{s}$ (see Example 16-2)
Vapor pressure of TCE	P_{vp}	60 mm Hg
Vapor pressure of water	P_{H_2O}	17.54 mm Hg
Diffusion coefficient of water vapor through air	D_{H_2O}	$0.239 \text{ cm}^2/\text{s}$
Initial concentration in soil (assumed)	c_o	0.05 g/cm^3
Adsorption coefficients (assumed)	α	1
	β	0
	K_{oc}	360
Solubility	S	1100 mg/L
Molecular weight	M	131.5 g/mole
Ratio $c_g/c_g (= S/\rho_{\max})$	K_H	$2.56 \text{ cm}^3 \text{ air/cm}^3 \text{ water}$
Environmental Characteristics (assumed)		
Humidity	h	0.5 (=50%)
Stagnant air layer thickness	δ	0.3 cm
Temperature	T	293K
Wind speed	v	100 cm/s
Soil solid density	ρ_{solid}	2.65 g/cm^3
Soil bulk density = $(1-\eta-\theta)\rho_{\text{solid}}$	ρ_b	1.32 g/cm^3
Volumetric soil water content	θ	$0.2 \text{ cm}^3/\text{cm}^3$
Soil air content	η	$0.3 \text{ cm}^3/\text{cm}^3$
Depth of soil column	L	20 cm
Water vapor flux per unit area	f_w	$6.7 \times 10^{-2} \text{ g/cm}^2/\text{day}$

a. Values for certain input parameters may be found in various chemistry and physics handbooks or in the published literature. This chapter and other chapters also provide estimation methods for some of the parameters.

- (3) The total loss (Q_t) over a given time period is the product of the flux and the time (in seconds). The total loss per day (86,400 s) is

$$\begin{aligned} Q_t &= (5.04 \times 10^{-5}) (86,400) \\ &= 4.4 \text{ g/cm}^2 \end{aligned}$$

Example 16-2 Hamaker Method, No Water Flux

- (1) The total loss of chemical per unit area is given by Eq. 16-8. This equation requires values for c_o and D . Table 16-5 lists the initial concentration, but the diffusion coefficient of TCE vapor through the soil (D) must be estimated. As in the preceding example, a reasonable estimate can be obtained by substituting known diffusion coefficients of other compounds in Eq. 16-5 and averaging the results. Table 16-6 lists vapor diffusion coefficients for various compounds at or near the desired temperature. (The diffusion coefficients used in the table were measured for conditions different from those assumed here; however, in the absence of other information we will assume that they are at least generally indicative of the desired value.) The final column lists the corresponding values of D for TCE as calculated from Eq. 16-5 and indicates an average of $0.039 \text{ cm}^2/\text{s}$.
- (2) Substituting the above in Eq. 16-8, the total loss of chemical per day (86,400 s) is

$$\begin{aligned} Q_t &= 2(0.05 \text{ g/cm}^3) \sqrt{(0.039 \text{ cm}^2/\text{s}) (86,400 \text{ s})/\pi} \\ &= 3.3 \text{ g/cm}^2 \end{aligned}$$

Example 16-3 Hamaker Method, Water Flux

- (1) In the case of water flux in the soil column, Hamaker's equation (Eq. 16-9) permits estimation of the TCE flux. The loss of liquid water will be neglected, so the $c(f_w)_L$ term is zero.
- (2) Substituting the values from Table 16-5 in Eq. 16-9,

$$\begin{aligned} Q_t &= \left(\frac{60 \text{ mm Hg}}{17.54 \text{ mm Hg}} \right) \left(\frac{0.072 \text{ cm}^2/\text{s}}{0.239 \text{ cm}^2/\text{s}} \right) (6.7 \times 10^{-2} \text{ g/cm}^2) + 0 \\ &= 6.9 \times 10^{-2} \text{ g/cm}^2 \end{aligned}$$

Example 16-4 Mayer/Letey/Farmer Method, No Water Flux (Model IV is used here to illustrate the five models in this method.)

- (1) An adsorption isotherm coefficient, R_o , relating c_{air} to c_{soil} must be known to use this model. R_o for TCE is apparently not available in the literature, but the parameter is known for lindane (3×10^{-5}) and dieldrin (2.4×10^{-6}). Using bounds of an order of magnitude either way will indicate the sensitivity of the estimated flux to these values.

TABLE 16-6

TCE Vapor Diffusion Coefficients Through Soil,
Calculated from Known Properties of Other Compounds Using Eq. 16-5
(See Example 16-2)

Chemical	M	D (cm ² /s)	T (K)	Soil	Soil Porosity	D _{TCE} (cm ² /s)
Ethylene Dibromide	187.9	0.015	293	Garden Soil	0.389	0.018
Ethylene Dibromide	187.9	0.005	293	Ashhurst	0.199	0.006
Ethylene Dibromide	187.9	0.011	293	Ashhurst	0.303	0.013
CO ₂	44	0.043	296	Dry	—	0.025
CS ₂	76	0.193	288.6	Dry Sand	0.374	0.147
Ethanol	46	0.0415	294.5	Dry Quartz Sand	0.415	0.025
O ₂	32	0.105	298	32.7% moist	0.38	0.052
O ₂	32	0.056	298	45.3% moist	0.27	0.028
Avg.						0.039

Source: Hamaker [7]

- (2) This model requires that the roots of Eq. 16-25 be found. Substituting the values of L , v , and D from Table 16-5, Eq. 16-25 becomes

$$\alpha_n \tan(20\alpha_n) = 100 R_o / 0.039$$

Insert values of R_o ranging from 3×10^{-4} to 2.4×10^{-7} and find the roots, α_n . A programmable calculator is helpful in this task. Table 16-7 lists the first 10 roots for four values of R_o . It is apparent that only a few roots may need to be evaluated, since the terms in the summation rapidly approach zero.

- (3) Equation 16-24 must now be solved to find the concentration in the soil. For the conditions of this example (Table 16-5), Eq. 16-24 becomes, for $z = 0$ (surface) and $t = 1$ day (86,400 s),

$$\begin{aligned} c(0, 1 \text{ day}) &= 2(0.05) \sum_{n=1}^{\infty} \frac{e^{-0.039 \alpha_n^2 (86,400)} R_o \left(\frac{100}{0.039} \right) \cos[\alpha_n (20 - 0)]}{(R_o / 0.039)^2 + \alpha_n^2 (20) + R_o \left(\frac{100}{0.039} \right)} \cos 20\alpha_n \\ &= 0.1 \sum_{n=1}^{\infty} \frac{128 R_o}{e^{3370 \alpha_n^2} (657 R_o^2 + 128 R_o + \alpha_n^2)} \end{aligned}$$

Substitution of the values of R_o and corresponding values of α_n in this equation result in the values for each term n in the summation listed in the s_n columns of Table 16-7. These terms are summed and multiplied by 0.1 to find the concentration in the soil for each R_o , as shown beneath the table.

- (4) In a similar manner, Eq. 16-26 is used to find the flux of TCE that volatilizes from the soil after one day. The following values result:

R_o	$f \text{ (g/cm}^2 \cdot \text{s)}$
3×10^{-4}	1.94×10^{-12}
3×10^{-5}	2.28×10^{-8}
2.4×10^{-6}	4.3×10^{-6}
2.4×10^{-7}	1.1×10^{-6}

This model is obviously quite sensitive to the value of R_o . At the upper limit of R_o (3×10^{-4}), the calculations show very small values of c and f after one day, indicating that most of the TCE has volatilized. At the lower limit of R_o , on the other hand, the surface concentration drops only 6% below the initial concentration in one day. Therefore, the value of R_o should be carefully chosen when this model is used. If this value is not available, model results are uncertain.

TABLE 16-7

Sample Calculations of Soil Concentration by Eq. 16-24
(See Example 16-4)

n	$R_o = 3 \times 10^{-4}$		$R_o = 3 \times 10^{-5}$		$R_o = 2.4 \times 10^{-6}$		$R_o = 2.4 \times 10^{-7}$	
	α_n	s_n^*	α_n	s_n^*	α_n	s_n^*	α_n	s_n^*
1	0.074	5.87×10^{-10}	0.0496	7.64×10^{-5}	0.0172	0.1771	0.00531	0.47
2	0.0784	6.1×10^{-11}	0.0784	2.39×10^{-10}	0.0784	4.79×10^{-11}	0.07844	4.9×10^{-12}
3	0.2216	1.9×10^{-73}	0.1778	5.08×10^{-48}	0.1591	1.09×10^{-39}	0.1572	8.5×10^{-40}
4	0.2353	8.5×10^{-83}	0.2350	9×10^{-83}	0.2353	5.23×10^{-84}	0.2353	5.3×10^{-85}
5	0.3703	0	0.3259	0	0.3153	0	0.3141	0
6	0.3928	0	0.3298	0	0.3928	0	0.3928	0
7	0.5203	0	0.479	0	0.4722	0	0.4716	0
8	0.5497	0	0.5497	0	0.5497	0	0.5497	0
9	0.6709	0	0.634	0	0.6291	0	0.6284	0
10	0.7066	0	0.7066	0	0.7066	0	0.7066	0
Σs_n		6.48×10^{-10}	7.6×10^{-5}		0.18		0.47	
c (0.1 day) g/cm ³		6.48×10^{-11}	7.6×10^{-6}		0.018		0.047	

* s_n are terms n of the summation in Eq. 16-24 (see step 3, Example 16-4).

Sources: Roots α_n found with TI-59 calculator Master Library program ML-08, "Zeros of Functions."

Example 16-5 Jury/Grover/Spencer/Farmer Method, No Water Flux

- (1) Although they are not needed for the flux calculation, the concentrations of TCE in the soil, soil water, and soil air may be of interest. From Eq. 16-32,

$$0.05 = 1.32 c_s + 0.2 c_l + 0.3 c_g$$

As stated in the assumptions made by Jury *et al*, $K_H = c_l/c_g$ and $c_s = \alpha c_l + \beta$.
Thus,

$$c_l = 2.56 c_g$$

and

$$c_s = 1 c_l$$

Solving the above equations for c_s , c_l , and c_g yields

$$c_s = 0.030 \text{ g/g}$$

$$c_l = 0.030 \text{ g/cm}^3$$

$$c_g = 0.012 \text{ g/cm}^3$$

- (2) The applicable flux equation is 16-41. The constant γ is defined as $\beta \rho_b$. Since β is 0, $\gamma = 0$.

- (3) The constant ϵ is defined as $\rho_b K_H \alpha + \theta K_H + \eta$. From Table 16-5,

$$\begin{aligned}\epsilon &= (1.32)(2.56)(1) + (0.2)(2.56) + 0.3 \\ &= 4.19\end{aligned}$$

- (4) In this model, c_g at $z = 0$ is always zero. Therefore, a value of $z = 1 \text{ cm}$ will be used to estimate gas-phase soil concentration.

- (5) D_e , the effective diffusion coefficient, is defined as $D_g + K_H D_l$. However, as D_g is usually orders of magnitude larger than D_l , $D_e = D_g$. This value was estimated earlier (Example 16-2) as $0.039 \text{ cm}^2/\text{s}$.

- (6) Substituting the above in Eq. 16-41, the gas-phase soil concentration at $t = 1 \text{ day}$ (86,400 s) and $z = 1 \text{ cm}$ is

$$\begin{aligned}c_g(1, 86400) &= \frac{0.05 - 0}{4.19} \operatorname{erf} \left(\frac{1}{2} \sqrt{(0.039)(86,400)/4.19} \right) \\ &= 0.012 \operatorname{erf}(14.2) \\ &= 0.012 \text{ g/cm}^3\end{aligned}$$

(Evaluation of the error function is described in §16-5.) Since this value of c_g is higher than the saturated vapor concentration, ρ_{\max} , of $4.3 \times 10^{-4} \text{ g/cm}^3$ (Table 16-5), this method of estimation may not be valid for the conditions of this example.

- (7) The flux is estimated by Eq. 16-44:

$$f(0,t) = -(0.05 - 0) \sqrt{\frac{0.039}{4.19 \pi (86,400)}}$$

$$= -9.3 \times 10^{-6} \text{ g/cm} \cdot \text{s}$$

The negative sign indicates that the flux is out of the soil column.

- (8) The total amount of TCE lost per day can be estimated from Eq. 16-47:

$$Q_t (1 \text{ day}) = 2 (0.05) \sqrt{\frac{0.039 \cdot 86,400}{\pi \cdot 4.19}}$$

$$= 1.6 \text{ g/cm}^2$$

This is a considerable amount, since in a 1-cm² soil column, TCE at 0.05 g/cm³ would have to be removed entirely to a depth of 32 cm in one day. This value for total loss again casts doubt on the validity of this model for chemicals other than those for which it was developed.

For comparison, c_g and $f(0,t)$ will be calculated by the water flux model (Eqs. 16-42 and -45). The only additional parameter needed is V_e .

- (9) From Table 16-5,

$$f_w = 6.7 \times 10^{-2} \text{ g/cm}^2/\text{day}$$

$$= 7.8 \times 10^{-7} \text{ g/cm}^2/\text{s}$$

- (10) V_e , the effective convection velocity, is defined as the product of f_w and K_H .

$$V_e = (7.8 \times 10^{-7})(2.56)$$

$$= 2.0 \times 10^{-6} \text{ cm/s}$$

- (11) By Eq. 16-42,

$$c_g(1, 86400) = \frac{0.05 - 0}{4.19} \left\{ 1 - \frac{1}{2} \operatorname{erfc} \left[\frac{1 + \frac{(2.0 \times 10^{-6})(86,400)}{4.19}}{2 \sqrt{(0.039)(86,400)/4.19}} \right] \right.$$

$$\left. - \frac{1}{2} e^{-(2.0 \times 10^{-6})(1)/0.039} \operatorname{erfc} \left[\frac{1 - \frac{(2.0 \times 10^{-6})(86,400)}{4.19}}{2 \sqrt{(0.039)(86,400)/4.19}} \right] \right\}$$

$$= 0.012 \left\{ 1 - \frac{1}{2} [1 - \operatorname{erf}(0.0184)] \right.$$

$$\left. - \frac{1}{2} e^{-(5.1 \times 10^{-5})} [1 - \operatorname{erf}(0.0173)] \right\}$$

$$= 1.3 \times 10^{-4} \text{ g/cm}^3$$

(Evaluation of the error function is described in § 16-5.)

(12) By Eq. 16-46,

$$w^2 = \frac{(2.0 \times 10^{-6})^2 (86,400)}{4 (0.039)} = 2.2 \times 10^{-6} \approx 0$$

(13) Then, by Eq. 16-45,

$$\begin{aligned} f(0,t) &= -(0.05 - 0) \sqrt{0.039/(\pi) (4.19) (86,400)} e^0 \\ &\quad - 2.0 \times 10^{-6} \left[\frac{0.05 - 0}{2 (4.19)} \right] [1 + \operatorname{erf}(1.49 \times 10^{-3})] \\ &= -9.3 \times 10^{-6} - (1.2 \times 10^{-8}) [1 + \operatorname{erf}(1.49 \times 10^{-3})] \\ &\approx -9.3 \times 10^{-6} \end{aligned}$$

Thus, both models give about the same results.

Example 16-6 Dow Method

(1) For a surface-applied chemical, the half-life on the surface can be estimated by Eq. 16-48.

$$\begin{aligned} t_{1/2} &= 1.58 \times 10^{-8} \left(\frac{360 \cdot 1100}{60} \right) \\ &= 1.0 \times 10^{-4} \text{ day} \\ &\approx 9 \text{ seconds} \end{aligned}$$

This half-life indicates that the chemical would probably volatilize soon after it was applied.

(2) The volatilization rate constant is found by Eq. 16-49:

$$\begin{aligned} k_v &= 0.693/1.0 \times 10^{-4} \\ &= 6.9 \times 10^3 \text{ day}^{-1} \end{aligned}$$

With k_v , the concentration of the chemical at any time can be found from the equation:

$$c = c_0 e^{-k_v t}$$

16-5 EVALUATING THE ERROR FUNCTION

The solution of some of the diffusion equations presented in this chapter requires the evaluation of the error function, $\text{erf}(x)$. The error function is defined as

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy \quad (16-51)$$

Since the error function involves an integral of the Gaussian or normal distribution, further information is usually found in standard reference texts on probability and statistics. Some of these texts contain tabulated values of $\text{erf}(x)$ for various values of x .

Four methods are presented below for evaluating $\text{erf}(x)$ without recourse to other works. They are:

- Method 1 — Tabulated values for $x \leq 2.2$ (Table 16-8)
- Method 2 — Graphical interpolation (Figure 16-6)
- Method 3 — Series expansion
- Method 4 — Approximations for:
 - (a) large x ($x \gtrsim 2$)
 - (b) intermediate x (values near 1)
 - (c) small x ($x \lesssim 0.1$)

It should be noted that $\text{erf}(-x) = -\text{erf}(x)$, and that values of $\text{erf}(x)$ range from 0 to +1 (0 to -1 for $\text{erf}(-x)$).

In particular:

$$\text{erf}(0) = 0 \quad (16-52)$$

and

$$\lim_{x \rightarrow \infty} (\text{erf}(x)) = 1 \text{ and } \lim_{x \rightarrow \infty} (\text{erf}(-x)) = -1 \quad (16-53)$$

Method 1. Table 16-8 provides values of $\text{erf}(x)$ for values of x up to 2.2. Values of $\text{erf}(x)$ are given for each 0.01 increment up to 1.5.

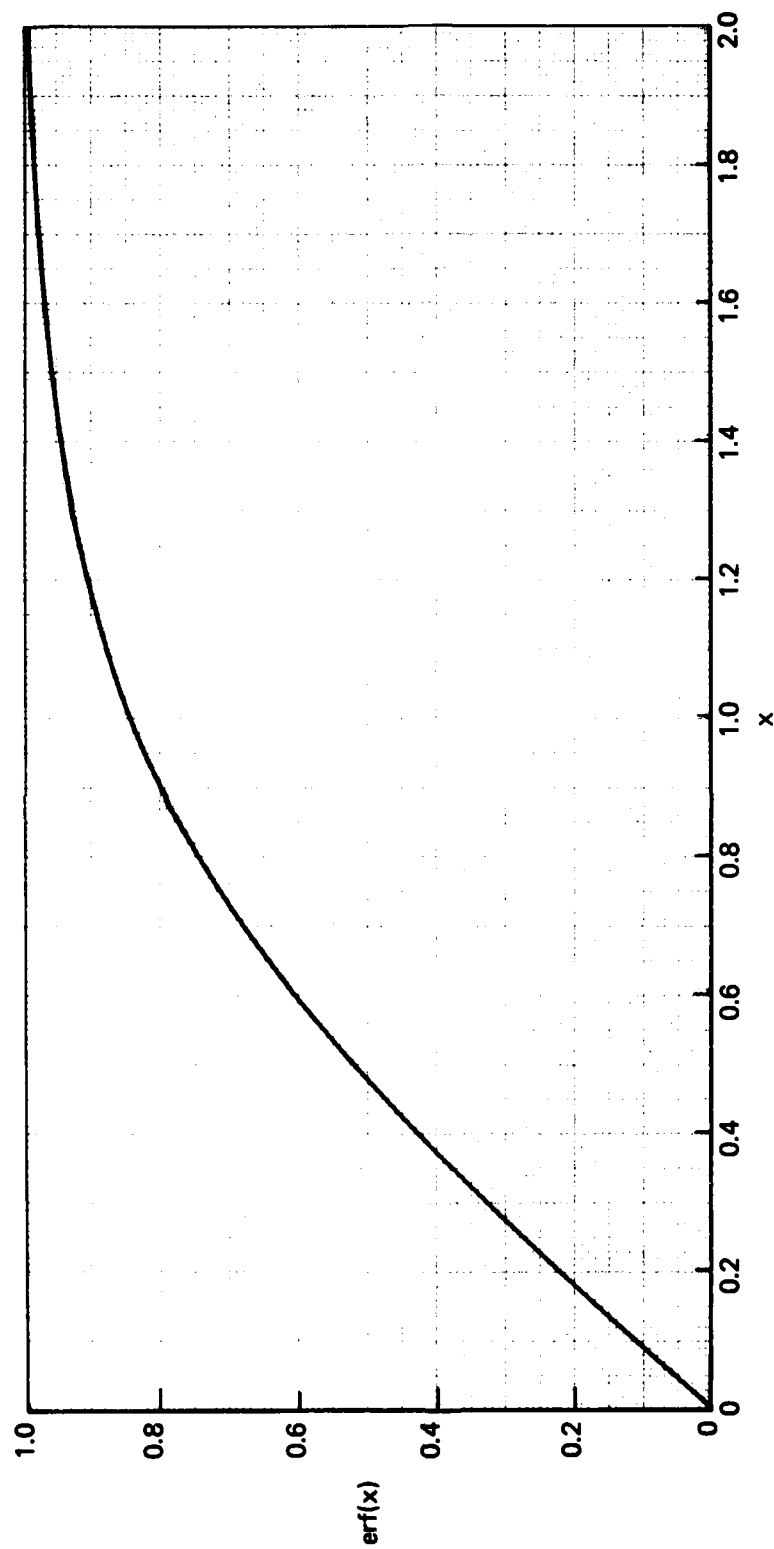
Method 2. Figure 16-6 is a plot of $\text{erf}(x)$ vs x for values of x up to 2.0. For values of x above 2, one can assume $\text{erf}(x) \approx 1.0$.

TABLE 16-8

Values of the Error Function for $x \leq 2.2$

x	0	1	2	3	4	5	6	7	8	9
0.0	0.0000	0.0113	0.0226	0.0338	0.0451	0.0564	0.0676	0.0789	0.0901	0.1013
0.1	0.1125	0.1236	0.1348	0.1459	0.1569	0.1680	0.1790	0.1900	0.2009	0.2118
0.2	0.2227	0.2335	0.2443	0.2550	0.2657	0.2763	0.2869	0.2974	0.3079	0.3183
0.3	0.3286	0.3389	0.3491	0.3593	0.3694	0.3794	0.3893	0.3992	0.4090	0.4187
0.4	0.4284	0.4380	0.4475	0.4569	0.4662	0.4755	0.4847	0.4937	0.5027	0.5117
0.5	0.5205	0.5292	0.5379	0.5465	0.5549	0.5633	0.5716	0.5798	0.5879	0.5959
0.6	0.6039	0.6117	0.6194	0.6270	0.6346	0.6420	0.6494	0.6566	0.6638	0.6708
0.7	0.6778	0.6847	0.6914	0.6981	0.7047	0.7112	0.7175	0.7238	0.7300	0.7361
0.8	0.7421	0.7480	0.7538	0.7595	0.7651	0.7707	0.7761	0.7814	0.7867	0.7918
0.9	0.7969	0.8019	0.8068	0.8116	0.8163	0.8209	0.8254	0.8299	0.8342	0.8385
1.0	0.8427	0.8468	0.8508	0.8548	0.8586	0.8624	0.8661	0.8698	0.8733	0.8768
1.1	0.8802	0.8835	0.8868	0.8900	0.8931	0.8961	0.8991	0.9020	0.9048	0.9076
1.2	0.9103	0.9130	0.9155	0.9181	0.9205	0.9229	0.9252	0.9275	0.9297	0.9319
1.3	0.9340	0.9361	0.9381	0.9400	0.9419	0.9438	0.9456	0.9473	0.9490	0.9507
1.4	0.9523	0.9539	0.9554	0.9569	0.9583	0.9597	0.9611	0.9624	0.9637	0.9649
1.5	0.9661	0.9672	0.9684	0.9695	0.9706	0.9716	0.9726	0.9736	0.9746	0.9755
1.6	0.9763					0.9804				
1.7	0.9838					0.9867				
1.8	0.9891									
1.9	0.9928									
2.0	0.9953									
2.1	0.9970									
2.2	0.9981									

Source: Jost [9]



Source: Potts *et al.* [14].

FIGURE 16-6 Error Function

Method 3. The series expansion given in Eq. 16-54 may be used to calculate erf (x) [5].

$$\text{erf } (x) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{n! (2n+1)} \quad (16-54)$$

In practice, only a few terms in the series must be added to obtain just two or three significant figures for erf (x). For example, summing the first five terms of Eq. 16-54 gives a value of erf (1) = 0.8434. The correct value of erf (1) is 0.8427.

Method 4. This method is based upon a more detailed description given in Ref. 2.

(a) For values of $x \geq 2$ use:

$$\text{erf } (x) \approx 1 - \frac{e^{-x^2}}{x\sqrt{\pi}} \quad (16-55)$$

where $e = 2.71828$ and $\pi = 3.14159$.

(b) For values of x close to 1, set $x = 1 + \nu$ ($\nu \ll 1$) and then use:

$$\text{erf } (x) \approx \text{erf } (1) + \frac{2\nu}{e\sqrt{\pi}} = 0.8427 + \frac{2\nu}{e\sqrt{\pi}} \quad (16-56)$$

(c) For values of $x \leq 0.1$ use:

$$\text{erf } (x) \approx \frac{2x}{\sqrt{\pi}} \quad (16-57)$$

16-6 SYMBOLS USED⁴

- c = concentration (M/L^3 or M/M)
- c_a = concentration in air (M/L^3)

4. Since most of the parameters are not restricted to particular units, only dimensions are given (M = mass, L = length, T = time).

- c_g = concentration in gas phase (in soil air) (M/L^3)
 c_l = concentration in liquid phase (M/L^3)
 c_o = initial concentration (M/L^3)
 c_s = concentration in soil (adsorbed) (M/L^3 or M/M)
 c_t = total concentration in soil (M/L^3)
 c_{t_o} = initial total concentration in soil (M/L^3)
 d = thickness of non-moving air layer in Eq. 16-27 (L)
 D = diffusion coefficient in soil in Eq. 16-1 (L^2/T)
 D_e = effective diffusion coefficient = $D_g + HDd$ in Eq. 16-38 (L^2/T)
 D_g = diffusion coefficient in gas phase (soil air) in Eq. 16-33 (L^2/T)
 D = diffusion coefficient in liquid phase (soil water) in Eq. 16-33 (L^2/T)
 D_s = nonvapor-phase diffusion coefficient in Eq. 16-1 (L^2/T)
 D_v = vapor-phase diffusion coefficient in air in Eq. 16-2 (L^2/T)
 D'_v = apparent vapor-phase diffusion coefficient in Eq. 16-1 (L^2/T)
 $\text{erf}(x)$ = error function of value x in Eq. 16-15 (see Table 16-8)
 $\text{erfc}(x)$ = complementary error function of value $x = 1 - \text{erf}(x)$ in Eq. 16-42 (see 16-5)
 f = flux of chemical in Eq. 16-6 ($M/L^2 \cdot T$)
 f_w = flux of water in Eqs. 16-9 and -33 ($M/L^2 \cdot T$)
 h = humidity of outer air in Eq. 16-6
 H = Henry's law constant
 k = thermal conductivity of air in Eq. 16-6 ($\text{cal}/L \cdot K$)
 k_v = rate constant for volatilization in Eq. 16-49 (T^{-1})
 K_H = constant for relating c_l and c_g , based on Henry's Law, = c_l/c_g ($\text{cm}^3 \text{ air}/\text{cm}^3 \text{ water}$)
 K_{oc} = soil adsorption coefficient (soil/water) in Eq. 16-48 ($(M/M)/(M/L^3)$)
 L = depth of soil column in Eq. 16-11 (L)
 m = exponent in Eq. 16-4
 M = molecular weight in Eq. 16-5 (M/mol)
 n = index in Eqs. 16-12 and -54
 P = ambient pressure in Eq. 16-1

P_o	=	reference pressure in Eq. 16-1
P_{vp}	=	vapor pressure of chemical in Eq. 16-9
Q_t	=	total loss of chemical/unit area in Eq. 16-9 (M/L^2)
R	=	universal gas constant
R_o	=	isotherm coefficient in Eq. 16-22
s	=	air-filled porosity in Eq. 16-2
s_t	=	total porosity in Eq. 16-2
S	=	solubility in Eq. 16-48 (M/L^3)
t	=	time (T)
$t_{1/2}$	=	half-life time in Eq. 16-48 (T)
T	=	temperature in Eq. 16-4
v	=	air velocity in Eq. 16-21 (L/T)
V	=	mean velocity of molecules in Eq. 16-4 (L/T)
V_e	=	effective convection velocity = $K_H f_w$ in Eq. 16-38
w	=	parameter in Eqs. 16-45, -46
x, y	=	parameters in Eq. 16-51
z	=	vertical (depth) coordinate in soil column (L)

Greek

α	=	parameter of adsorption isotherm in Eq. 16-35
α_n	=	root of Eq. 16-23
β	=	parameter of adsorption isotherm in Eq. 16-35
γ	=	$\beta \rho_b$ in Eq. 16-36
δ	=	thickness of stagnant layer in Eq. 16-6 (L)
ϵ	=	$(\rho_b K_H \alpha + \theta K_H + \eta)$ in Eq. 16-36
η	=	soil air content in Eq. 16-32 (L^3/L^3)
θ	=	volumetric soil water content in Eq. 16-32 (L^3/L^3)
λ_v	=	latent heat of vaporization in Eq. 16-6 (cal/M)
ν	=	parameter in Eq. 16-56
π	=	3.14159
ρ	=	vapor density in Eq. 16-2 (M/L^3)
ρ_b	=	soil bulk density in Eq. 16-2 (M/L^3)
ρ_{max}	=	saturated vapor concentration at the temperature of the outside air in Eq. 16-6 (M/L^3)

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17

DIFFUSION COEFFICIENTS IN AIR AND WATER

William A. Tucker and Leslie H. Nelken

17-1 INTRODUCTION

Molecular diffusion is the net transport of a molecule in a liquid or gas medium and is a result of intermolecular collisions rather than turbulence or bulk transport. The process is promoted by *gradients*, such as pressure, temperature, and concentration, the last of which is considered in this chapter. The rate of diffusion is a function of the properties of two compounds; i.e., it depends not only on the nature of the compound in question but also on the medium through which the compound moves. The *diffusion coefficient*, or diffusivity, is defined as

$$\mathcal{D}_{BA} = \frac{J_B}{\nabla X_B} \quad (17-1)$$

where \mathcal{D}_{BA} = diffusion coefficient of compound B in compound A
(cm²/s)
 J_B = net molal flux of B across a hypothetical plane
(mol/cm²·s)
 ∇X_B = concentration gradient of B at the hypothetical plane
(mol/cm³·cm)

A cursive \mathcal{D} is used to distinguish this property from the *apparent* diffusion coefficient, which is typically represented by D . The compo-

nents that comprise the binary system are indicated by subscripts to the symbol; in this chapter, one of the components is always air (A) or water (W).

It should be emphasized that the methods described in this chapter are *not* useful for estimating the dispersion¹ of contaminants in either the atmosphere or surface water bodies. Most environmental fluid media — the atmosphere, rivers, lakes and oceans — are turbulent, and dispersion in these media is therefore controlled by the intensity of turbulent mixing rather than molecular diffusion. For example, in meteorological or oceanographic literature, the apparent dispersion coefficient, turbulent diffusion coefficient, diffusivity, or dispersivity (denoted by D_e in this chapter) all refer to the ratio of the contaminant flux to its gradient; in turbulent flow, this coefficient is always much greater than the molecular diffusion coefficient, D_{BA} .

Even in highly stable layers of the atmosphere, such as inversions or in thermoclines of oceans and lakes, actual transfer rates are significantly higher than they would be if caused solely by molecular diffusion. Although these stabilized layers are usually laminar flow regions, intermittent bursts of turbulence caused by flow instabilities account for most of the dispersion through them [9]. Published coefficients of dispersion, turbulent diffusion, or eddy diffusion in the atmosphere or surface waters are generally several orders of magnitude larger than the diffusion coefficients derivable by the methods explained in this chapter.

There are, however, several special environmental situations in which molecular diffusion is a significant, or even controlling, factor in determining chemical fluxes. These include air-water interfaces, the interstitial waters of sediments, and groundwater (saturated or unsaturated soils).

Air-Water Interfaces. The air-water interface is probably the most important of the fluid interfaces considered in environmental analyses. Its thickness, which varies according to the rate of turbulent mixing in the free fluids, has a direct effect on the transfer rate for a given chemical.

Even when the rate of turbulent mixing is constant and the thickness of the interface does not change, however, the transfer rate varies from one chemical to another. This is because of the action of the laminar boundary layers on both sides of the interface; in these boundary layers,

1. The combined effect of molecular diffusion and contaminant migration associated with fluid motion.

turbulence is suppressed, and the flux of chemicals across the fluid-fluid (or fluid-solid) interface is largely a process of molecular diffusion. Thus, chemicals with different molecular diffusion coefficients exhibit different interfacial fluxes.

This relationship has prompted the method of Smith *et al.* [22,23], which relates the fluxes of gases across the surface of rivers and lakes to the reaeration rate constant (oxygen mass transfer coefficient). The flux of a chemical is approximately equal to the oxygen transfer rate times the ratio of the chemical's diffusion coefficient to that of oxygen. (See Eq. 15-20.) The formulation established by Smith *et al.* is a special case of the more general relationship presented by Kraus [8], who derived a gas-phase exchange coefficient, k_g , that characterizes the rate of diffusion in cm/s across the molecular boundary layers.² For the air side,

$$k_g = \frac{D_{AB} U}{75 \nu_A} \quad (17-2)$$

where ν_A is the kinematic viscosity of air at 20°C (0.15 cm²/s), and U is the wind speed (cm/s) at a height of 10 meters. The water-phase exchange coefficient is given by:

$$k_l = \frac{D_{WB} U}{75 \nu_W} \sqrt{\frac{\rho_A}{\rho_W}} \quad (17-3)$$

where ν_W is the kinematic viscosity of water (0.01 cm²/s) and ρ_A and ρ_W are the density of air and water (at 20°C), respectively. This water-phase exchange coefficient is valid only when momentum is transferred from air to water, as in lakes, oceans, and slowly flowing streams. For rapidly flowing water, the water current becomes a factor.

Liss and Slater [12] and Liss [11] have further developed this concept, defining the overall interfacial resistance to transfer as

$$R_T = \frac{1}{k_l} + \frac{1}{H'k_g} \quad (17-4)$$

where H' is the Henry's law constant. This approach is described in more detail in Chapter 15. Equation 17-4 implies that transfer is limited by water phase exchange when $k_l < H'k_g$.

2. Kraus used the term "diffusion velocity" instead of "phase exchange coefficient." The latter is used here to keep the terminology consistent with that of Chapter 15.

Interstitial Waters. Other environmental media where molecular diffusion can be important include groundwaters and the interstitial waters of sediments, where the movement of water is not turbulent. However, the flow paths of molecules through porous media are not parallel as in typical laminar flow because of the tortuous path taken through the pore spaces; these meandering flow paths through the porous medium are analogous to the eddy motion of a turbulent fluid, causing the observed dispersivities to exceed molecular diffusion rates. In many instances, particularly when the water moves slowly, the molecular diffusion coefficient affects the overall dispersion process. In a recent review of exchange at the sediment-water interface, Lerman [10] discusses data of Manheim [14] which indicate that the ratio of the apparent diffusion coefficient to the molecular diffusion coefficient varies as the sediment porosity raised to the n th power, where $1.2 < n < 2.8$.

The vertical distribution of anthropogenic contaminants in undisturbed lake, estuarine, or ocean sediments reflects historical contaminant loadings to the water body. The analysis of potential contaminant migration in the interstitial waters after deposition requires an analysis of molecular diffusion in the aqueous phase of the sediments.

Groundwater. In saturated groundwater (aquifers) the effective dispersivity is generally much greater than the molecular diffusion coefficient. Scheidigger [20] postulated that the apparent dispersivity is proportional to the flow velocity and that molecular diffusion may therefore be significant in aquifer systems with extremely slow flow rates. Rifai *et al.* (1956) (cited in Ref. 7) determined that molecular diffusion is important at pore water velocities of less than 2.5×10^{-4} cm/s, in saturated flow. Harleman and Rumer (1962) (also cited in Ref. 7) proposed the following relationship:

$$D_s = f_t \mathcal{D}_{BW} + \alpha u^m \quad (17-5)$$

where D_s = apparent dispersion coefficient (cm^2/s)
 f_t = the tortuosity factor, a soil property (0.01-0.5)
 u = pore water velocity (cm/s)
 α, m = empirically determined soil constants

Scheidigger's theoretical analysis suggests $m=1$, while empirically determined values range from 1 to 1.4 [3]. Kirda *et al.* [7] found that the ratio of D_s to \mathcal{D}_{BW} is greater than 100 for $u > 0.002$ cm/s. Therefore, molecular diffusion can probably be ignored at pore water velocities exceeding 0.002 cm/s.

The analysis is more complicated in unsaturated soils, since these represent a three-phase system consisting of soil particles, water, and air. Liquid-phase and gas-phase diffusion, as well as diffusion along the water-air and water-solid interfaces, contribute to dispersion. (Air-solid interfaces are of lesser importance, because any available water will exist as a coating on soil particles and minimize their contact with the air.) Two equations (17-6 or 17-8) have been developed for describing dispersion in these cases, assuming there is no net infiltration of water into the soil. The more rigorous, by Shearer *et al.* [21], yields the following expression for the effective diffusion coefficient (D_{EF}):

$$D_{EF} = \frac{\mathcal{D}_{AB} p^{7/3}}{p_T^2 (S+1)} + \left(\frac{S}{1+S} \right) \left(\frac{D_S + D_H K' \beta + \beta D_I S'}{\beta K' + \theta + \beta S'} \right) \quad (17-6)$$

- where
- \mathcal{D}_{AB} = gas diffusion coefficient in air (cm^2/s)
 - p = air-filled porosity of the soil ($0-0.7 \text{ cm}^3/\text{cm}^3$)
 - p_T = total porosity of the soil ($0-0.7 \text{ cm}^3/\text{cm}^3$)
 - S = equilibrium coefficient of proportionality between vapor mass density and total concentration of pesticide in soil (g/cm^3)/(g/cm^3)
 - D_S = apparent solution phase diffusion coefficient (cm^2/s)
 - D_H = apparent diffusion coefficient of molecules adsorbed at the solution-solid interface (cm^2/s)
 - K' = adsorption coefficient (cm^3/g)
 - β = soil bulk density (g/cm^3)
 - D_I = apparent diffusion coefficient of molecules adsorbed at the air-solution interface (cm^2/s)
 - S' = coefficient of proportionality between solution concentration and vapor concentration at the air-solution interface (cm^3/g)
 - θ = fractional volumetric water content (cm^3/cm^3)

Furthermore, it was shown in Ref. 19 that

$$D_S = (\theta/p_T)^2 \theta^{4/3} \mathcal{D}_{BW} \quad (17-7)$$

but the authors did not derive similar theoretical expressions for D_H and D_I .

Walker and Crawford [25] developed the following equation for use when liquid-phase diffusion is assumed to predominate:

$$D_{EF} = \frac{\mathcal{D}_{BW} \theta f_t}{\beta K' + \theta} \quad (17-8)$$

For this case, where $\mathcal{D}_{BA} = D_H = D_I = S' = 0$, Shearer's expression (Eq. 17-6) reduces to

$$D_{EF} = \frac{S [(\theta/p_T)^2 \theta^{4/3} \mathcal{D}_{BW}]}{(1+S)(\beta K' + \theta)} \quad (17-9)$$

Clearly, by either analysis, the effective diffusion coefficient is proportional to the molecular diffusion coefficient and inversely proportional to the term $(\beta K' + \theta)$. Available information does not permit a comparative evaluation of these different expressions relating the effective diffusion coefficient to the molecular diffusion coefficient.

17-2 DIFFUSIVITY IN AIR

Methods for estimating the diffusion coefficient of a binary gas system have foundations in the theoretical equation derived independently by Chapman and Enskog (cited in Ref. 17) for dilute gases at low pressures. They found that the diffusion of gases by intermolecular collision is a function of Boltzmann's constant (k), the molecular weight as described by M_r , the collision integral (Ω), and the characteristic length (σ_{AB}) of molecule A interacting with molecule B, according to the following equation:

$$\mathcal{D}_{AB} = 1.858 \times 10^{-3} \left(\frac{T^{3/2} \sqrt{M_r}}{P \sigma_{AB}^2 \Omega} \right) \quad (17-10)$$

where $M_r = (M_A + M_B)/M_A M_B$
 P = pressure (atm)
 T = temperature (K)

This equation was derived for non-polar, monatomic spherical molecules and has since been tested on a number of organic gases over a wide temperature range. Values of Ω and σ_{AB} are functions of temperature and depend upon the intermolecular potential function selected. For this chapter, the Lennard-Jones 12-6 potential is used [17].

Empirical equations for estimating the diffusion coefficient reflect much of the Chapman-Enskog equation form. The equation of Wilke and

Lee [28], for example, differs only in the constant (1.858×10^{-3}), which is expressed as a function of the molecular weight.

The gaseous diffusion coefficient is a function of density, pressure, and temperature. It is inversely related to density and pressure; the product of $\mathcal{D}_{BA}\rho$ decreases with increasing density, while the product $\mathcal{D}_{BA}P$ is nearly constant at low pressures [17].

The gaseous diffusion coefficient is theoretically related to temperature (T) in the following manner:

$$\mathcal{D}_{BA} \propto \frac{T^{3/2}}{\Omega(T)} \quad (17-11)$$

The exponential coefficient for temperature varies from 1.5 to 2 over a wide temperature range. Among recommended methods, the Wilke and Lee (WL) method uses 1.5; Fuller, Schettler and Giddings (FSG) uses 1.75, which Barr and Watts [1] found to give the best value for the gaseous diffusion coefficient. The WL method retains the temperature-dependent collision integral function and therefore allows for prediction of \mathcal{D}_{BA} with good accuracy over a wide temperature range. The FSG method does not incorporate any temperature-dependent functions to compensate for the fixed exponential coefficient associated with T, so the diffusion coefficient calculated by this method is accurate only over a limited temperature range; however, as the temperature range encountered in environmentally important systems is not very wide, the accuracy is normally adequate.

17-3 AVAILABLE METHODS OF ESTIMATING DIFFUSION COEFFICIENTS IN AIR

A number of methods exist for estimating the gaseous diffusion coefficient. Jarvis and Lugg [6,13] compared the results of nine estimation techniques with measured diffusion coefficients for approximately 150 compounds in air. For the most part, these methods require few data inputs. Only two of the methods listed in Table 17-1 require critical properties; the others use readily available or easily estimated data. The method errors shown in the table, except for that of Venezian [24], were calculated from the findings of Jarvis and Lugg. Although the reported absolute average errors do not differ greatly, a few of the methods listed are applicable only to a limited number of chemical groups. The two recommended methods are described in the following section.

TABLE 17-1
Methods for Estimating Gaseous Diffusion Coefficients

Method	Inputs (excluding air parameters)	Applicability	Compounds Tested (n)	Absolute Average Error (%)	% n ≤ ± 5% Error	Comments
Fuller, Schettler and Giddings ^{a, b}	M _B , V _B	Applicable to nonpolar gases at low to moderate temperatures	128	7.6	42	Does not distinguish isomers
Wilke and Lee ^a	M _B , σ _{AB} , Ω	Applicable to a wide range of compounds and temperatures	137	4.3	69	See notes c and d. Does not distinguish isomers
Chen and Othmer ^e	M _B , T _{CB} , V _{CB}	Unsuitable for amides and amines	66	4.0	76	Requires critical properties
Gilliland	M _B , V _B	Applicable only to restricted range of compounds	151	10	26	Does not distinguish isomers
Arnold	M _B , V _B		151	8.9	54	
Hirschfelder, Bird and Spotz	M _B , σ _{AB} , Ω	Greatest accuracy for aliphatic esters, acids, alcohols	151	9.3	16	See notes c and d. Accuracy increases with increasing molecular weight
Andrusson	M _B , V _B , P	Accurate only for substituted aromatics and glycols	151	9.1	33	Does not distinguish isomers. Deviations observed were most erratic of methods using molar volume
Othmer and Chen	M _B , V _{CB}		66	8.3	25	Requires critical parameters
Venezian [24]	M _B , n _D		28	9.1		

a. Recommended method.

b. Calculations used experimental atomic diffusion data.

Source: Jarvis and Lugg [6] except where noted.

c. $\sigma_{AB} = f(V'_B)$.

d. $\Omega = f(T, \epsilon_{AB})$.

e. From Ref. 2 except for error analysis, which is from Ref. 6.

17-4 SELECTED METHODS OF ESTIMATING GASEOUS DIFFUSION COEFFICIENTS OF ORGANICS IN AIR

The criteria for choosing a specific estimation technique include (1) ease of use, (2) availability of input data, and (3) accuracy of results for a general chemical population. Of those listed in Table 17-1, only the first two fulfill all of these requirements. Both methods estimate the gaseous diffusion coefficient from the structure of the chemical, although neither can distinguish between isomers.

The FSG method is much easier and less time-consuming than the WL method and is reportedly applicable to non-polar gases at low to moderate temperatures. Jarvis and Lugg [6] state that the method is most accurate for chlorinated aliphatics and that aromatics, alkanes, and ketones deviate $\pm 5\%$ from the measured value. It does not give accurate estimates for esters and alcohols higher than C_6 and C_7 , respectively. The reported average absolute error of 7.6% is based on values of the atomic diffusion volume, a parameter which is derived from measured diffusion coefficient values.

The WL method, as mentioned earlier, is very similar to the theoretical expression derived by Chapman and Enskog and is applicable to many kinds of compounds over a fairly wide temperature range. It is a much more tedious computation, since parameters such as the collision integral and characteristic length must be calculated by additional approximations. However, as shown in Table 17-2, the average errors obtained with this method are considerably less than those of the FSG method for some classes of chemicals, particularly nitriles, glycols, and aromatic esters.

FSG Method. The method of Fuller, Schettler and Giddings [4] is most accurate for non-polar gases at low to moderate temperatures. Its accuracy is poorest with the polar acids and glycols (Table 17-2); minimal error is associated with the aliphatics and aromatics. The method is based on the following correlation:

$$D_{BA} = \frac{10^{-3} T^{1.75} \sqrt{M_r}}{P (V_A^{1/3} + V_B^{1/3})^2} \quad (17-12)$$

TABLE 17-2

Comparison of Absolute Average Errors by Chemical Class

	Number of Compounds Tested	WL Method (%)	FSG Method (%)
Aliphatics	3	1.8	3.9
Aromatics	13	3.9	4.2
Substituted Aromatics	9	4.2	9.9
Alcohols	17	5.8	9.6
Ethers	5	6.1	7.5
Ketones	5	1.4	3.0
Acids	8	8.7	12.4
Aliphatic Esters	36	3.9	8.5
Aromatic Esters	4	1.8	9.8
Halogen Hydrocarbons	22	3.4	1.7
Glycols	7	1.0	11.5
Amines and Amides	6	7.6	4.3
Nitriles	2	1.9	7.8

Source: Jarvis and Lugg [6]

where T and M_r are as previously defined, P is the pressure (atm), and V_A and V_B are the molar volumes for air and the gas in question, respectively. Values for V_A and other properties of air are listed in Table 17-3. V_B can be estimated from the chemical structure of the molecule using the increments listed in Table 17-4. For a chemical containing atoms that are not listed in Table 17-4, the diffusion volume can be estimated as 85-90% of the LeBas volume, V'_B [17], i.e.,

$$V_B \approx (0.85 \text{ to } 0.90)V'_B \quad (17-13)$$

Increments for calculating LeBas volumes are listed in Table 17-5. (See description of the WL method below.) The molal volumes of some chemicals, notably organophosphorus compounds, cannot be estimated from either Table 17-4 or 17-5 because the related atoms are not listed.

Basic Steps

- (1) Find M_B , the molecular weight of gas B.
- (2) Use Table 17-3 to find M_A and V_A .
- (3) Calculate M_r from $(M_A + M_B)/M_A M_B$.

TABLE 17-3

Some Physical Properties of Air

M_A	28.97 g/mol
V_A	20.1 cm ³ /mol
ϵ/k	78.6 K
σ_A	3.711 Å

Source: Jarvis and Lugg [6]. Values of ϵ/k and σ_A obtained from Lennard-Jones 12-6 potential function.

TABLE 17-4

Atomic and Structural Diffusion Volume Increments^a
(cm³/mol)

	ΔV_B
C	16.5
H	1.98
O	5.48
N	(5.69)
Cl	(19.5)
S	(17.0)
Aromatic and heterocyclic rings	— 20.2

a. Values in parentheses are based upon few data points.

Source: Fuller, Schettler, and Giddings [4].

TABLE 17-5

Additive Volume Increments for Calculating
LeBas Molar Volume, V'_B

Atom	Increment (cm ³ /mol)	Atom	Increment (cm ³ /mol)
C	14.8	Br	27.0
H	3.7	Cl	24.6
O (except as noted below)	7.4	F	8.7
In methyl esters and ethers	9.1	I	37.0
In ethyl esters and ethers	9.9	S	25.6
In higher esters and ethers	11.0	Ring	
In acids	12.0	3-Membered	— 6.0
Joined to S, P, N	8.3	4-Membered	— 8.5
N		5-Membered	—11.5
Double bonded	15.6	6-Membered	—15.0
In primary amines	10.5	Naphthalene	—30.0
In secondary amines	12.0	Anthracene	—47.5

Source: Reid *et al.* [17]

- (4) Calculate V_B by adding the incremental values for the atoms listed in Table 17-4; for molecules containing atoms not listed in this table (except P), calculate the LeBas volume, V'_B , from Table 17-5 and use 87.5% of this value as the atomic diffusion volume.
- (5) Calculate \mathcal{D}_{BA} using Eq. 17-12 for the temperature and pressure (P) of interest. P will usually be 1 atm.

Example 17-1 Calculate the diffusion coefficient of *m*-chlorotoluene (C_7H_7Cl) into air at 25°C and 1 atm, given $M_B = 126.59$ g/mol.

- (1) From Table 17-3,

$$M_A = 28.97 \text{ g/mol and } V_A = 20.1 \text{ cm}^3/\text{mol}$$

- (2) Calculate M_r

$$M_r = (28.97 + 126.59)/(28.97)(126.59) = 0.0424$$

- (3) Calculate V_B for *m*-chlorotoluene from Table 17-4:

$$\begin{aligned} 7(C) &= 7(16.5) \\ 7(H) &= 7(1.98) \\ 1(Cl) &= 1(19.5) \\ 1(\text{Ring}) &= 1(-20.2) \\ V_B &= 128.7 \text{ cm}^3/\text{mol} \end{aligned}$$

- (4) Using Eq. 17-12,

$$\mathcal{D}_{BA} = \frac{10^{-3} (298)^{1.75} \sqrt{0.0424}}{1 \cdot [(20.1)^{1/3} + (128.7)^{1/3}]^2} = 7.31 \times 10^{-2} \text{ cm}^2/\text{s}$$

The deviation is +13% from the literature value, $6.45 \times 10^{-2} \text{ cm}^2/\text{s}$ [6].

Example 17-2 Calculate the diffusion coefficient of isopropyl iodide $((CH_3)_2CHI)$ into air at 25°C and 1 atm, given $M_B = 169.9$ g/mol.

- (1) Since $M_A = 28.97$ g/mol (Table 17-3), M_r is:

$$M_r = (28.97 + 169.9)/(28.97)(169.9) = 0.0404$$

- (2) V_B of $(CH_3)_2CHI$ cannot be determined by using Table 17-4. The LeBas volume (Table 17-5) is:

$$\begin{aligned} 3(C) &= 3(14.8) \\ 7(H) &= 7(3.7) \end{aligned}$$

$$l(I) = \frac{1(37.0)}{1}$$

$$V'_B = 107.3 \text{ cm}^3/\text{mol}$$

$$\text{Thus, } V_B \approx 0.875 \times 107.3 = 93.9 \text{ cm}^3/\text{mol}.$$

(3) From Eq. 17-14

$$D_{BA} = \frac{10^{-3} (298)^{1.75} \sqrt{0.0404}}{1 \cdot [(20.1)^{1/3} + (93.9)^{1/3}]^2} = 8.15 \times 10^{-2} \text{ cm}^2/\text{s}$$

The literature value is $8.78 \times 10^{-2} \text{ cm}^2/\text{s}$ [6], indicating a deviation of -7.2% .

WL Method. The method of Wilke and Lee [28] for estimating gaseous diffusion coefficients is reported to be usable for a wider range of compounds and temperatures than is the FSG method. According to Jarvis and Lugg [6], the absolute average error for about 150 compounds tested was 4.3%; all classes of compounds had average errors of less than 8%, except for acids. (See Table 17-2.) This method is significantly more accurate than the FSG method for nitriles, aromatic esters, and glycols.

The correlation used is very similar to that developed by Chapman and Enskog (see Eq. 17-10):

$$D_{BA} = \frac{B'T^{3/2} \sqrt{M_I}}{P\sigma_{AB}^2 \Omega} \quad (17-14)$$

where

$$B' = 0.00217 - 0.00050 \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \quad (17-15)$$

The other parameters are as defined for Eq. 17-10. The greater accuracy is obtained at the cost of more tedious computation, involving calculation of the parameters Ω and σ_{AB} .

The collision integral, Ω , is a function of the molecular energy of attraction, ϵ , and the Boltzmann constant, k , as shown in Eqs. 17-16 and 17 [17].

$$\Omega = \frac{a}{(T^*)^b} + \frac{c}{e^{T^*d}} + \frac{e}{e^{T^*f}} + \frac{g}{e^{T^*h}} \quad (17-16)$$

where the values of a-h are as follows:

$$\begin{array}{llll} a = 1.06036 & c = 0.19300 & e = 1.03587^a & g = 1.76474 \\ b = 0.15610 & d = 0.47635 & f = 1.52996 & h = 3.89411 \end{array}$$

$$T^* = \frac{T}{(\epsilon/k)_{AB}} \quad (17-17)$$

The denominator of Eq. 17-17 is defined as

$$(\epsilon/k)_{BA} = \sqrt{(\epsilon/k)_A (\epsilon/k)_B} \quad (17-18)$$

where $(\epsilon/k)_A = 78.6K$ (Table 17-3) and, from Ref. 28,

$$(\epsilon/k)_B = 1.15 T_b \text{ (K)} \quad (17-19)$$

The characteristic length, σ_{AB} , is a function of the molal volume at the boiling point:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \quad (17-20)$$

where $\sigma_A = 3.711 \text{ \AA}$ (Table 17-3) and, from Ref. 28,

$$\sigma_B = 1.18 (V'_B)^{1/3} \quad (17-21)$$

Thus, calculation of Ω and σ_{AB} ultimately requires knowledge of the molecular weight, boiling point, and molal volume of compound B. If the boiling point is unknown, it can be estimated by methods presented in Chapter 12, and the LeBas method (Table 17-5) provides a means of estimating molal volume.

Basic Steps

- (1) Retrieve the molecular weight and boiling point (K) of the compound from the literature.
- (2) From Table 17-3, obtain M_A , $(\epsilon/k)_A$, and σ_A .
- (3) Calculate the LeBas molal volume (V'_B) for the compound of interest using Table 17-5.
- (4) Substitute V'_B in Eq. 17-21 to find σ_B .

3. The constant e is used only once in Eq. 17-16. The e 's printed in bold face are the base of natural logarithms (2.718+).

- (5) Calculate σ_{AB} from Eq. 17-20.
- (6) Use Eq. 17-19 to determine $(\epsilon/k)_B$ from T_b .
- (7) Calculate T^* for the desired temperature by using Eq. 17-18 and 17-17 in that order.
- (8) Insert T^* and constants a-h in Eq. 17-16 for evaluation of Ω .
- (9) Find B' from Eq. 17-15.
- (10) Calculate $(M_A + M_B)/M_A M_B$ to obtain M_r .
- (11) Calculate \mathcal{D}_{BA} from Eq. 17-14, using the known values of T and P and the derived values of B' , M_r , σ_{AB} , and Ω .

Example 17-3 Calculate the diffusion coefficient of *m*-chlorotoluene (C_7H_7Cl) in air at 25°C (298K) and 1 atmosphere.

- (1) From the literature, $M_B = 126.59$ g/mol, and $T_b = 435K$.

- (2) From Table 17-3,

$$M_A = 28.97 \text{ g/mol}$$

$$\sigma_A = 3.711 \text{ \AA}$$

$$(\epsilon/k)_A = 78.6K$$

- (3) From Table 17-5, the increments of the LeBas molal volume are:

$$7(C) = 7(14.8) = 103.6$$

$$7(H) = 7(3.7) = 25.9$$

$$1(Cl) = 24.6$$

$$6\text{-membered ring} = -15.0$$

$$V'_B = 139.1 \text{ cm}^3/\text{mol}$$

- (4) From Eq. 17-21,

$$\sigma_B = 1.18(139.1)^{1/3} = 6.11 \text{ \AA}$$

- (5) From Eq. 17-20,

$$\sigma_{AB} = (3.711 + 6.11)/2 = 4.91 \text{ \AA}$$

- (6) From Eq. 17-19,

$$(\epsilon/k)_B = 1.15(435) = 500K$$

- (7) From Eq. 17-18,

$$(\epsilon/k)_{AB} = \sqrt{(78.6)(500)} = 198K$$

which yields the following (Eq. 17-17):

$$T^* = 298/198 = 1.51$$

(8) From Eq. 17-16,

$$\begin{aligned}\Omega &= \frac{1.06}{1.51^{0.156}} + \frac{0.193}{e^{(1.51)(0.476)}} + \frac{1.04}{e^{(1.51)(1.53)}} + \frac{1.76}{e^{(1.51)(3.89)}} \\ &= 1.20\end{aligned}$$

(9) From Eq. 17-15,

$$\begin{aligned}B' &= 0.00217 - 0.00050 \sqrt{(1/28.97) + (1/126.59)} \\ &= 2.07 \times 10^{-3}\end{aligned}$$

$$\begin{aligned}(10) \quad M_T &= (28.97 + 126.59)/(28.97)(126.59) \\ &= 0.0424\end{aligned}$$

(11) From Eq. 17-14,

$$\begin{aligned}D_{BA} &= \frac{(2.07 \times 10^{-3})(298)^{3/2} \sqrt{0.0424}}{(1)(4.91)^2(1.20)} \\ &= 7.58 \times 10^{-2} \text{ cm}^2/\text{s}\end{aligned}$$

This value deviates +17.5% from the literature value of $6.45 \times 10^{-2} \text{ cm}^2/\text{s}$ [6].

Example 17-4 Calculate the diffusion coefficient of isopropyl iodide, $(\text{CH}_3)_2\text{CHI}$, in air at 298K and 1 atmosphere.

- (1) From the literature, $M_B = 169.9 \text{ g/mol}$ and $T_b = 362.45\text{K}$.
- (2) The values of M_A , σ_A and $(\epsilon/k)_A$ are as given in Example 17-3.
- (3) From Table 17-5, the increments of the LeBas molal volume are:

$$\begin{aligned}3(\text{C}) &= 3(14.8) = 44.4 \\ 7(\text{H}) &= 7(3.7) = 25.9 \\ 1(\text{I}) &= \underline{37} \\ V'_B &= 107.3 \text{ cm}^3/\text{mol}\end{aligned}$$

- (4) $\sigma_B = 1.18(107.3)^{1/3} = 5.61 \text{ \AA}$ (Eq. 17-21)
- (5) $\sigma_{AB} = (3.71 + 5.61)/2 = 4.66 \text{ \AA}$ (Eq. 17-20)
- (6) $(\epsilon/k)_B = 1.15(362.45) = 417\text{K}$ (Eq. 17-19)
- (7) $(\epsilon/k)_{AB} = \sqrt{(417)(78.6)} = 181.0\text{K}$ (Eq. 17-18)

Therefore,

$$T^* = 298/181 = 1.65 \text{ (Eq. 17-17)}$$

(8) Substituting the above values in Eq. 17-16, $\Omega = 1.15$

$$\begin{aligned} (9) \quad B' &= 0.00217 - 0.00050 \sqrt{(1/28.97) + (1/169.9)} \\ &= 2.07 \times 10^{-3} \text{ (Eq. 17-15)} \end{aligned}$$

$$\begin{aligned} (10) \quad M_r &= (28.97 + 169.9)/(28.97)(169.9) \\ &= 0.0404 \end{aligned}$$

$$\begin{aligned} (11) \quad \mathcal{D}_{BA} &= \frac{(2.07 \times 10^{-3})(298)^{3/2} \sqrt{0.0404}}{(1)(4.66)^2(1.15)} \\ &= 8.57 \times 10^{-2} \text{ cm}^2/\text{s} \end{aligned}$$

This deviates -2.4% from the literature value of $8.78 \times 10^{-2} \text{ cm}^2/\text{s}$ [6].

17-5 DIFFUSIVITY IN WATER

Equation 17-22, the theoretically derived Stokes-Einstein equation, is the foundation of existing methods for estimating the liquid diffusion coefficient.

$$\mathcal{D}_{BW} \approx \frac{RT}{6 \eta_w r_B} \quad (17-22)$$

where η_w = viscosity of water (cp)
 r_B = radius of molecule B (cm)

This equation applies to large, spherical molecules diffusing in a continuous solution (i.e., one consisting of small molecules) [17]. The correlation equations that have been developed for \mathcal{D}_{BW} are generally functions of solute size, temperature, and solution viscosity. A number of researchers [17] have found that \mathcal{D}_{BW} is not simply proportional to the inverse of viscosity, as suggested by Eq. 17-22; rather, it is more closely correlated to η raised to a power between -0.45 and -0.66. The deviation from the Stokes-Einstein equation is caused by variations in molecular shape and size.

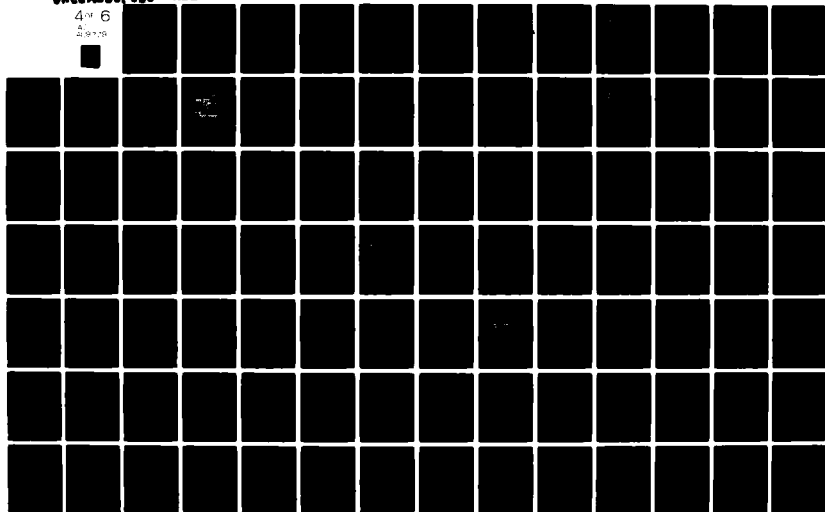
The dependence of \mathcal{D}_{BW} upon temperature over a wide range has not been sufficiently studied for firm conclusions to be reached [17]. The correlation of viscosity, with temperature suggests that \mathcal{D}_{BW} is similarly dependent, since $\mathcal{D}_{BW}\eta/T$ remains constant when T changes; over the

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small temperature range typically encountered in the environment, however, a nonlinear temperature dependence of \mathcal{D}_{BW} should be insignificant.

The methods presented in this chapter assume that diffusion of the organic compound occurs in an infinitely dilute solution, or at least where the concentration of solute is less than 0.05 molar. The actual diffusion coefficient, D_{BW} (i.e., where the solute concentration >0.05 molar) is observed to be a function of the activity and mole fraction of the solute. Reid *et al.* [17] provide a detailed explanation of the methods proposed to compensate for the effects of concentration on \mathcal{D}_{BW} . They conclude by recommending the following equation suggested by Vignes:

$$D_{BW} = (\mathcal{D}_{WB})^{X_B} (\mathcal{D}_{BW})^{X_W} \quad (17-23)$$

where X_W and X_B are the mole fractions of water and compound B. A plot of $\log D_{BW}$ vs. mole fraction should be linear and give data that can be used for concentrated binary liquid systems.

17-6 AVAILABLE METHODS FOR ESTIMATING DIFFUSION COEFFICIENTS IN WATER

Table 17-6 summarizes six methods for estimating the liquid diffusion coefficient. The Wilke-Chang method [27] incorporates a solution association constant (ϕ), which is a function of the solution polarity. Wilke and Chang assigned a value of 2.6 for aqueous solutions, fitting experimental data published prior to 1950. They calculated an average error of 10% for an unspecified number of compounds. Using a data set of more recently measured values, Hayduk and Laudie [5] found that an association parameter of 2.26 reduced the average error to 5.8%.

The method of Scheibel [19] requires the molal volumes of both the solute and solvent. Scheibel theorized that the mechanism of diffusion is a function of the relative sizes of the molecules comprising a liquid binary system; unlike the Wilke-Chang equation, Scheibel's equation does not take solution polarity into account. Nevertheless, Hayduk and Laudie determined that Scheibel's method results in an absolute average error slightly smaller than that of Wilke-Chang.

The last two methods listed in Table 17-6 are not recommended here because of (1) their numerous input parameters, (2) lack of general applicability to aqueous solutions, and/or (3) relatively low accuracy.

TABLE 17-6
Available Methods for Estimating Diffusivity into Water

Method [Ref.]	Formula	Inputs (excluding water parameters)	Absolute Average Error (%) [5]
Hayduk and Laudie [5] ^a	$D_{BW} = \frac{13.26 \times 10^{-5}}{\eta_W^{1.14} V_B^{0.589}}$	V_B	5.8 (87 solutes)
Wilke-Chang [27]	$D_{BW} = \frac{7.4 \times 10^{-8} (\phi_W M_W)^{1/2} T}{\eta_W V_B^{0.5}}$	V_B	8.8 (87 solutes)
Scheibel [19]	$D_{BW} = \frac{8.2 \times 10^{-8} T}{\eta_W V_B^{1/3}} \left[1 + \left(\frac{3V_W}{V_B} \right)^{2/3} \right]$	V_B	6.7 (87 solutes)
Othmer and Thakar [5]	$D_{BW} = \frac{1.4 \times 10^{-5}}{\eta_W^{1.1} V_B^{0.5}}$	V_B	5.9 (87 solutes)
Reddy and Doraiswamy [17] ^b	$D_{BW} = \frac{M_W^{1/2} T K'}{\eta_W (V_W V_B)^{1/3}}$	V_B	< 20 (96 solutes)
Venezian [24]	$D_{BW} = \frac{6 \times 10^{-10} T}{\eta_W (R_M - 0.855)}$ where $R_M = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \left(\frac{M_B}{\rho_B} \right)^{1/3}$	η_D, ρ_B, M_B	

a. Recommended method. b. $K' = 10 \times 10^{-8}$ for $V_W/V_B \leq 1.5$ and 8.5×10^{-8} for $V_W/V_B > 1.5$.

The following section describes the computation method of Hayduk and Laudie, which is a modification of the Othmer-Thakar equation. Further discussion of Scheibel's and Wilke and Chang's methods is not warranted, since they do not require unique input parameters and are not quite as accurate as the Hayduk and Laudie method.

17-7 RECOMMENDED METHOD OF ESTIMATING \mathcal{D}_{BW} FOR ORGANIC LIQUIDS AND VAPORS

The Hayduk and Laudie method for estimating the diffusion coefficient of organic compounds in water is comparable to the Wilke-Chang and Scheibel methods in terms of input parameters, accuracy, and general applicability to a wide range of compounds. This method has been recommended by Reid *et al.* [17] because its computation is slightly easier than that required by the latter two methods, and because it has been validated by a more recently compiled data base.

The Hayduk and Laudie method is based on the following equation:

$$\mathcal{D}_{BW} = \frac{13.26 \times 10^{-5}}{\eta_W^{1.14} V_B'^{0.589}} \quad (17-24)$$

Unlike the previously mentioned correlations, Eq. 17-24 does not include a temperature term, since temperature dependence is incorporated in the viscosity term [5]. Hayduk and Laudie report an average absolute error of 5.8% for 87 solutes diffusing into water, using the LeBas method for molal volume, as is recommended below.

Basic Steps

- (1) From Table 17-7 obtain the viscosity of water, η_w , at the desired temperature.
- (2) Calculate V_B' by the LeBas method, summing the applicable incremental values listed in Table 17-5.
- (3) Substitute the above values of η_w and V_B' in Eq. 17-24 and compute the diffusion coefficient.

Example 17-5 Compute the diffusion coefficient of aniline ($C_6H_5NH_2$) in water at 25°C.

- (1) From Table 17-7, η_w at 25°C = 0.8904 cp

TABLE 17-7

Viscosity of Water at Various Temperatures

°C	η_w (cp)	°C	η_w (cp)	°C	η_w (cp)
0	1.787	11	1.271	21	0.9779
1	1.728	12	1.235	22	0.9548
2	1.671	13	1.202	23	0.9325
3	1.618	14	1.169	24	0.9111
4	1.567	15	1.139	25	0.8904
5	1.519	16	1.109	26	0.8705
6	1.472	17	1.081	27	0.8513
7	1.428	18	1.053	28	0.8327
8	1.386	19	1.027	29	0.8148
9	1.346	20	1.002	30	0.7975
10	1.307				

Source: Weast and Astle [26].

- (2) From Table 17-5,

$$6(C) = 6(14.8) = 88.8$$

$$7(H) = 7(3.7) = 25.9$$

$$1(N\text{-primary amine}) = 10.5$$

$$1(6\text{-membered ring}) = -15.0$$

$$V'_B = 110.2 \text{ cm}^3/\text{mol}$$

- (3) From Eq. 17-24,

$$\mathcal{D}_{BW} = \frac{13.26 \times 10^{-5}}{(0.8904)^{1.14} (110.2)^{0.589}} = 0.95 \times 10^{-5} \text{ cm}^2/\text{s}$$

This estimate deviates -10% from the literature value of $1.05 \times 10^{-5} \text{ cm}^2/\text{s}$ [5].**Example 17-6** Compute the diffusion coefficient of ethyl acetate ($\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$) in water at 25°C.

- (1) From Table 17-7,
- η_w
- at 25°C = 0.8904 cp

- (2) From Table 17-5,

$$4(C) = 4(14.8) = 59.2$$

$$8(H) = 8(3.7) = 29.6$$

$$2(O) = 2(9.9) = 19.8$$

$$V'_B = 108.6 \text{ cm}^3/\text{mol}$$

(3) From Eq. 17-24,

$$D_{BW} = \frac{13.26 \times 10^{-5}}{(0.8904)^{1.14} (108.6)^{0.589}} = 0.96 \times 10^{-5} \text{ cm}^2/\text{s}$$

This deviates - 14% from the measured value of $1.12 \times 10^{-5} \text{ cm}^2/\text{s}$ [5].

17-8 AVAILABLE DATA

Measured values of diffusion coefficients may be found in Refs. 5, 13, and 15. Values of M and T_b required as inputs for the recommended methods are readily available from sources such as those listed in Appendix A.

17-9 SYMBOLS USED

a through h = constants in Eq. 17-16

B' = constant in Eqs. 17-14, -15

= theoretical diffusion coefficient (cm^2/s)

D = apparent diffusion coefficient (cm^2/s)

D_a = apparent dispersion coefficient in Eq. 17-5 (cm^2/s)

D_s = apparent solution phase diffusion coefficient in Eq. 17-6 (cm^2/s)

f_t = tortuosity factors in Eqs. 17-5 and -8

H = Henry's law constant in Eq. 17-4

J = flux in Eq. 17-1 ($\text{mol}/\text{cm}^2\text{-s}$)

k = Boltzmann's constant = $1.38062 \times 10^{-16} \text{ ergs/K}$

k_g = gas-phase exchange coefficient in Eq. 17-2 (cm/s)

k_l = liquid-phase exchange coefficient in Eq. 17-3 (cm/s)

K' = adsorption coefficient in Eq. 17-6

M = molecular weight (g/mol)

M_r = $(M_A + M_B)/M_A M_B$. (Note that the M_r used here is the reciprocal of what is usually called the reduced mass.)

m = soil constant in Eq. 17-5

n_D = refractive index in method of Venezian (Table 17-4)

p = air-filled porosity in Eq. 17-6 (cm^3/cm^3)

p_T = total porosity in Eq. 17-6 (cm^3/cm^3)

P = pressure (atm)

r = molecular radius in Eq. 17-22 (cm)

R	= gas constant
R_m	= constant in method of Venezian (Table 17-6)
R_r	= overall interfacial resistance to transfer in Eq. 17-4
S	= proportionality constant of vapor density to solution concentration in Eq. 17-6
S'	= equilibrium constant at air/solution interface in Eq. 17-6
T	= temperature (K)
T*	= constant in Eqs. 17-16, -17
u	= pore water velocity in Eq. 17-5 (cm/s)
U	= wind velocity in Eqs. 17-2, -3 (cm/s)
v	= atomic diffusion volume (cm ³ /mol)
V	= molar volume (Schroeder method) (cm ³ /mol)
V'	= molar volume (LeBas method)
X	= mole fraction
∇X	= concentration gradient in Eq. 17-1 (mol/cm ³ · cm)

Greek

α	= soil constant in Eq. 17-5
β	= soil bulk density in Eq. 17-6
ε	= molecular energy of attraction (ergs)
η	= viscosity (cp)
θ	= volumetric water content in Eq. 17-6
ν	= kinematic viscosity in Eq. 17-2 (cm ² /s)
ρ	= density (g/cm ³)
σ	= characteristic length of molecule (Å)
φ	= solution association constant in Wilke-Chang equation
Ω	= collision integral in Eq. 17-10

Subscripts

A	= air
B	= compound B
c	= critical property
EF	= effective (diffusion) in Eq. 17-6
I	= air/solution interface in Eq. 17-6

H = solution/solid interface in Eq. 17-6
 T = total porosity
 W = water

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18

FLASH POINTS OF PURE SUBSTANCES

John H. Hagopian

18-1 INTRODUCTION

The flash point of a substance is commonly defined [8] as the minimum temperature at which it emits sufficient vapor to form an ignitable mixture with air near its surface or within the chamber of a testing apparatus. An "ignitable mixture" is in turn defined as a fuel-air mixture within the explosive range (i.e., with a gaseous fuel concentration in air between the lower and upper flammability limits of the fuel) that is capable of propagating flame away from a source of ignition.

Although flash points are normally associated with flammable or combustible liquids, they are also useful for characterizing solids that sublime, as they indicate the relative ease with which substances can be ignited at a given temperature. Typical measured values range from -36°F (-38°C) for acetaldehyde to 450°F (232°C) for diisooctyl phthalate.¹

In theory, the flash point of a pure substance in equilibrium with its vapors is the temperature at which the vapor concentration equals the lower flammable limit (LFL) or lower explosive limit (LEL) concentration at standard atmospheric pressure. Several estimation methods take advantage of this fact to provide "ideal" or equilibrium flash points.

1. These are closed-cup flash points, cited simply as examples. Flash points measured in other ways and for other substances may have higher or lower values.

Most flash points listed in the literature have been experimentally determined in one or more of several types of testing apparatus. Among these are the Tag Closed Tester, the Pensky-Martens Closed Tester, the Setaflash Closed Tester, the Cleveland Open Tester, and the Tag Open Tester. Standard specifications for these units are published by the American Society for Testing and Materials (ASTM). Results from the first three types are referred to as "closed-cup" flash points, while those from the latter two types are called "open-cup" flash points.

Because of differences in equipment design and testing procedure, the numerical value of the closed-cup flash point is typically some 5-10°F lower than that of the open-cup flash point for the same liquid. The difference can be greater or smaller in particular cases, however, depending on the particular apparatus used, the purity of the substance, and the degree of equilibrium achieved. It is not surprising, therefore, that the literature often reports a number of different closed-cup and open-cup flash points for the same substance, all of which may differ from the "ideal" or equilibrium flash point.

All of the estimated methods presented in this chapter take advantage of a general relationship between the flash points and normal boiling points of a homologous series of liquids. Affens [1] used vapor pressure and lower flammable limit data for n-alkanes to define equilibrium flash points and, ultimately, an equation for estimating flash point as a function of boiling point. Prugh [12] generalized and simplified the approach, at some loss in accuracy, to cover a wide variety of organic substances and developed a nomograph. Butler *et al.* [5] simply used experimentally derived closed-cup flash points and normal boiling points to develop a relationship for pure hydrocarbons, and Hagopian [6] extended this work, developing similar relationships for aldehydes, amines, ketones, and alcohols.

A different method, by Shimy [13], is not presented here, primarily because of its limited applicability. It requires an intermediate calculation of the autoignition temperature,² using the total number of carbon atoms in the molecule and the number of carbon atoms in branches. The flash point is then calculated with an expression that contains the autoignition temperature and the number of hydrogen atoms in radicals. The method applies only to paraffinic hydrocarbons, olefins, the benzene series, and alcohols.

2. The autoignition temperature, sometimes simply called the "ignition temperature," is the minimum temperature at which a material will ignite without a spark or flame being present. The ASTM provides a standard method for its measurement.

18-2 SELECTION OF APPROPRIATE METHOD

Table 18-1 lists recommended methods of estimation, indicates the kinds of substances to which they apply, and comments upon their bases and overall accuracy. Further details are given in the following sections.

It is difficult, if not impossible, to assess the accuracy of any of the methods. Since flash point data in the literature are derived experimentally and often span a range of temperatures for any given substance, and since the results of the estimation methods can be compared only with these values, it is entirely possible that a given method is more or less accurate than noted in Table 18-1 or the following text. Indeed, comments on the overall accuracy of any given method are intended only to give a rough approximation for the general case.

With many substances, more than one method can be used. For example, both Prugh's nomograph and the equation of Butler *et al.* can be used for pure hydrocarbons, and the nomograph can be used for other types of substances addressed by this author. In such cases, it is recommended that all pertinent methods be applied. If the results are comparable, they are probably fairly accurate; if they are not comparable, the estimates can be compared with literature values for similar substances with slightly higher or lower boiling points. Since higher boiling points generally suggest higher flash points, a significantly erroneous estimate should be immediately evident.

18-3 AFFENS' METHOD

Principles of Use. Affens [1] utilized actual curves of vapor pressure versus temperature together with experimentally derived lower flammability limits to estimate the equilibrium flash points for n-alkanes with 1 to 14 carbon atoms. Using boiling point data, he then plotted boiling points versus flash points and found the line that best fit these points. The line corresponded to the equation:

$$t_f = 0.6946 t_b - 122.9 \quad (18-1)$$

where t_f is the flash point and t_b is the normal boiling point, both in degrees Fahrenheit. The equation does not work well for methane; for other n-alkanes in the series, however, it predicts flash points generally within 9°F (5°C) of an average of flash points reported in the literature.

What is most useful here is not the equation, since the flash points of the n-alkanes are fairly well defined in the literature, but the basic

TABLE 18-1
Overview of Flash Point Estimation Methods

Method	Applicability	Basis	Accuracy
Affens [1]	Provides equilibrium flash points for n-alkanes.	Uses actual vapor pressure and LFL data to determine flash points graphically. Basic methodology can be applied to other types of substances.	Generally within 9°F (5°C) of literature value and within 4°F (2°C) of precisely computed equilibrium flash points for n-alkanes with 2 to 14 carbon atoms.
Prugh [12]	Provides closed-cup flash points for pure organic compounds containing carbon, hydrogen, oxygen, sulfur, and halogens.	Nomograph based on estimates of LFL and vapor pressure data, along with actual data for 200 chemicals.	Author claims nomograph yields predictions within 20°F (11°C).
Butler [5]	Provides closed-cup flash points for pure hydrocarbons. Normal paraffins, cycloparaffins, aromatics, and sharply separated fractions all fit the given equation.	Based on relationship between actual flash-point and boiling-point data for similar substances. Basic methodology can be applied to other types of substances.	Not specifically expressed. Of 29 points on graph presented, 24 are within 14°F (8°C) of equation curve. Maximum error is 40°F (22°C) for tetralin.
Hagopian [6]	Provides both open- and closed-cup flash points for alcohols, aldehydes, amines, and ketones.	Same as Butler <i>et al.</i> [5].	Average errors range from 5.2°F (2.9°C) to 17.0°F (9.4°C), depending on combination of flash point and material type.

methodology for estimating equilibrium flash points for pure substances.³ This is described below.

Basic Steps

- (1) Plot vapor pressure versus temperature for the substance, using literature data or one of the estimation methods given in Chapter 14. The result will correspond to curve A in Figure 18-1.

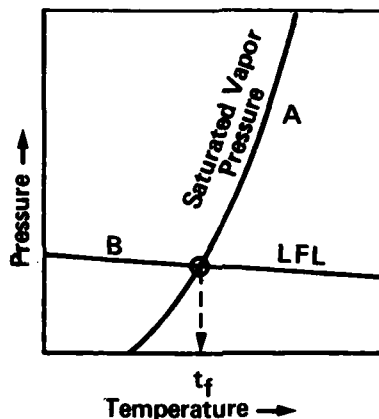


FIGURE 18-1 Graphical Determination of Equilibrium Flash Point

- (2) Find the lower flammable limit (LFL) or lower explosive limit (LEL) of the substance in the literature. (Some sources are listed in §18-7.) These data are usually given in units of volume percent. It is preferable to obtain sufficient data to plot a curve of LFL or LEL as a function of temperature, if such data are available.
- (3) Convert the LFL or LEL data to the same units as the vapor pressure data. The equation for converting from volume percent to mm Hg is:

$$\text{LFL (mm Hg)} = \frac{760}{100} \times \text{LFL (vol \%)} \quad (18-2)$$

- (4) Plot the LFL or LEL data in units of pressure on the same graph with the vapor pressure data, as in curve B of Figure 18-1. The intersection of the two curves indicates the equilibrium flash point, t_f , of the substance. If only a single value of LFL or LEL is obtainable, as will frequently be the

3. This and subsequent methods generally apply when the flash point of the substance is below the temperature at which it begins to decompose.

case, find the temperature that corresponds to it on the vapor pressure curve. Since LFL and LEL are generally not strong functions of temperature, the loss in accuracy should not be great.

Example 18-1 Find the equilibrium flash point of n-hexane, given data on its saturated vapor pressure and lower flammability limit from Ref. 1 as functions of temperature.

- (1) Plot the vapor pressure data. The result is shown in curve A of Figure 18-2.
- (2) Plot the LFL data after converting from volume percent to mm Hg with Eq. 18-2. The result is shown as curve B.
- (3) The intersection of curves A and B indicates that the equilibrium flash point of n-hexane (t_f) is approximately -14°F . In comparison, Ref. 16 lists a closed-cup value of -7°F , and Ref. 1 gives -9.4°F as an average of literature values.

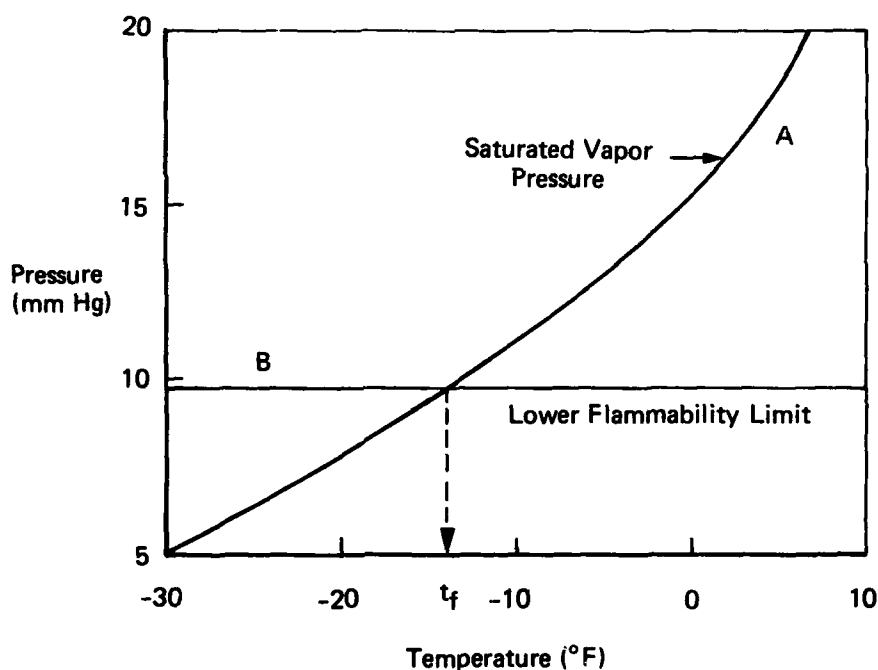


FIGURE 18-2 Determination of Equilibrium Flash Point of n-Hexane by Affens' Method

18-4 PRUGH'S METHOD

Principles of Use. Prugh [12] made a number of generalizations that permit prediction of the vapor pressure versus temperature curves and

lower flammability or explosive limits of organic compounds solely on the basis of their normal boiling points and chemical structures. Subsequently, he utilized the definition of equilibrium flash point, together with actual data for 200 chemicals, to develop a nomograph and a procedure for its use.

Prugh's nomograph is presented in Figure 18-3. The procedure that he recommended for its use is as follows:

Basic Steps

- (1) Calculate the stoichiometric concentration x_{st} of the vapor in air from the equation:

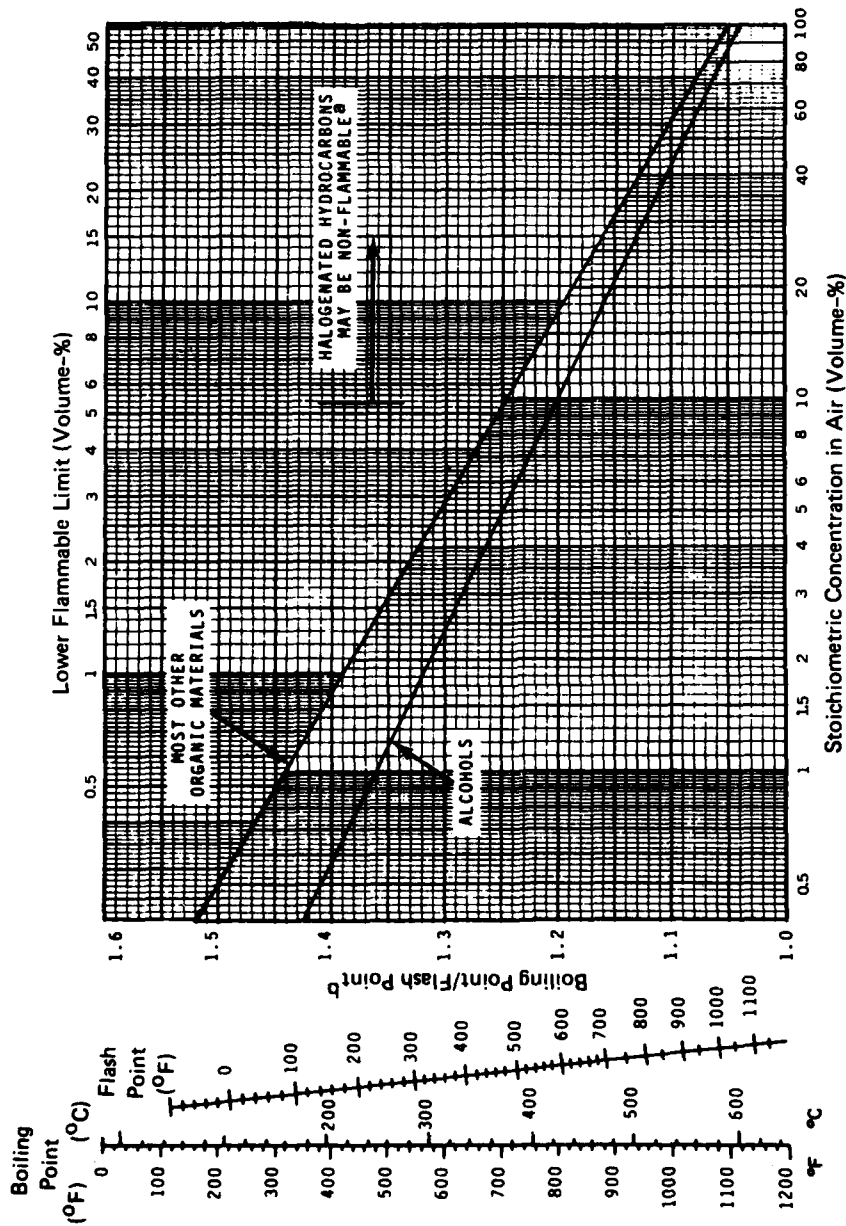
$$x_{st} = \frac{83.8}{4(C) + 4(S) + (H) - (X) - 2(O) + 0.84} \text{ vol \%} \quad (18-3)$$

where C, S, H, X, and O are respectively the number of carbon, sulfur, hydrogen, halogen, and oxygen atoms in the molecule of fuel.

- (2) Find the point on the appropriate line for "alcohols" or "most other organic materials" on Figure 18-3 that corresponds to the stoichiometric concentration computed above.
- (3) Mark the "boiling-point/flash-point" scale (the vertical axis of the graph) at the location corresponding to this point.
- (4) Mark the boiling-point scale (i.e., the left-most scale) at the appropriate boiling point.
- (5) Connect the points marked in steps (3) and (4).
- (6) Read the approximate flash point where the connecting line intersects the flash-point scale between the boiling-point scale and the left axis of the graph.⁴

Prugh states that the nomograph will yield flash points within approximately 20°F (11°C) of the correct value. To check the validity of the nomograph further, the author of this chapter extracted values for 14 compounds at random from a handbook and compared them with predictions. The overall average error was 7.5°F (4.2°C). Seven of the predictions (50%) were within 3°F (1.7°C) of the literature value, four (29%) were within 5-10°F (2.8-5.6°C), two were within 15-20°F (8.3-16.7°C),

4. Although not explicitly stated, this scale probably indicates closed-cup flash points, since the data in the referenced source are mostly of this kind.



- Fuel molecules containing a relatively large number of halogen atoms may not be flammable and may actually be fire extinguishing agents.
- The temperatures in this ratio must be expressed in degrees Rankine ($^{\circ}R$)

Source: Prugh [12]

FIGURE 18-3 Nomograph for Estimation of Flash Point

and one was 25°F (13.9°C) in error. Since results were found to be sensitive to slight variations in the position of marks and connecting lines, the user is advised to be as precise as possible.

Example 18-2 Estimate the flash point of methyl butyrate, given a boiling point of 215°F (101.7°C) and a chemical formula of $\text{CH}_3\text{OOCCH}_2\text{CH}_2\text{CH}_3$.

- (1) The molecule contains 5 carbon atoms, 10 hydrogen atoms, and 2 oxygen atoms. From Eq. 18-3.

$$X_{st} = \frac{83.8}{(4 \times 5) + 0 + 10 - 0 - (2 \times 2) + 0.84} = 3.12 \text{ vol } \%$$

- (2) Find the value of X_{st} on the bottom axis of the graph in Figure 18-3 and proceed upward vertically to the line labeled "Most Other Organic Materials."
- (3) Proceed horizontally to the left axis of the graph and mark the "boiling point/flash point" scale at the appropriate value. For this example, the appropriate value is 1.343.
- (4) Draw a line between this point and 215°F on the boiling-point scale.
- (5) The intersection of the drawn line with the flash-point scale provides a flash-point estimate in the range of 50-55°F. For comparison, the handbook value is 57°F.

18-5 BUTLER'S METHOD

Principles of Use. Butler *et al.* [5] plotted the flash points of pure hydrocarbons (values obtained by means of the Pensky-Martens closed-cup flash point tester) against their respective normal boiling points and then fit a curve through the points. The equation corresponding to this curve was:

$$t_f = 0.683 t_b - 119 \quad (18-4)$$

where t_f is the flash point and t_b is the normal boiling point, both in degrees Fahrenheit. The boiling points considered ranged from 150°F (66°C) to 550°F (288°C).

The available data did not indicate any great variation among hydrocarbon types. Normal paraffins, cycloparaffins, aromatics, and sharply defined fractions all fit the above equation fairly well. Of 29 points on the graph presented, 24 were within approximately 14°F (8°C) of the curve; the maximum deviation was approximately 40°F (22°C).

Hagopian [6] used the same method to develop relationships for the open- and closed-cup flash points of assorted alcohols, aldehydes, amines, and ketones with varying degrees of success. Table 18-2 presents the resulting equations, together with ancillary data describing degree of error, number of data sets used, temperature range addressed, and other details.

As with Affens' method, the technique for developing the equations is of greater significance than the equations themselves. The basic steps are outlined below.

Basic Steps

- (1) From the literature, find the normal boiling points and flash points of substances similar to that for which a flash-point prediction is desired.
- (2) Plot the flash points versus the associated boiling points on regular graph paper.
- (3) Fit the best curve through the points.
- (4) Use the normal boiling point of the substance in question to find its flash point from the curve.

In general, there appear to be no great variations between the flash-point characteristics of any specific homologous series of substances and other series within the same basic chemical family. This was indicated by Butler's findings, as well as by those of Hagopian. Nevertheless, it is probably advisable to use data only for substances within exactly the same homologous series, if sufficient data are available.

The curve through the points on the resulting graph can either be "eyeballed" or fitted by means of numerical regression. While the latter approach is more complicated, it obviously provides a more precise fit with the data.

Example 18-3 Find the closed-cup flash point of acetaldehyde ($t_b = 68.7^\circ\text{F}$).

- (1) The appropriate equation in Table 18-2 is:

$$t_f = 0.6901 t_b - 92.3$$

- (2) Substitution of the boiling point in this equation gives:

$$t_f = 0.6901 (68.7) - 92.3 = -44.9^\circ\text{F}$$

In comparison, the handbook value of the closed-cup flash point is -36°F .

TABLE 18-2
Flash Point Estimation Equations

Chemical Family	Type of Measurement	Number of Data Points Used	Boiling Point Range (°F)	Equation ^a	Average Deviation (°F)	Maximum Deviation (°F)
Alcohols	Closed cup	31	180 ^b to 491	$t_f = 0.7056 t_b - 77.1$	6.7	14.2
	Open cup	25	180 ^b to 506	$t_f = 0.6875 t_b - 66.4$	7.4	18.5
Aldehydes	Closed cup	8	69 to 329	$t_f = 0.6901 t_b - 92.3$	6.9	13.9
	Open cup	17	69 to 469	$t_f = 0.7491 t_b - 107.8$	5.8	18.9
Amines	Closed cup	19	120 to 531	$t_f = 0.7962 t_b - 120.9$	17.0	38.6
	Open cup	22	90 to 532	$t_f = 0.7988 t_b - 114.2$	13.3	41.1
Ketones	Closed cup	18	133 to 433	$t_f = 0.6717 t_b - 95.2$	8.0	20.4
	Open cup	17	133 to 425	$t_f = 0.6917 t_b - 89.7$	5.2	16.1

a. Both t_f and t_b must be expressed in degrees Fahrenheit.

b. Extrapolation below this temperature will produce erroneous results.

Source: Hagopian [6].

Example 18-4 Find the flash point of a substance, given the flash points and normal boiling points for compounds within the same chemical family.

- (1) Plot the flash points against associated boiling points as in Figure 18-3.
- (2) Draw a curve through the points. (The best fit is not always a straight line.)
- (3) Find t_f for the substance in question by using its normal boiling point and the curve drawn. The dashed lines on Figure 18-4 demonstrate the procedure.

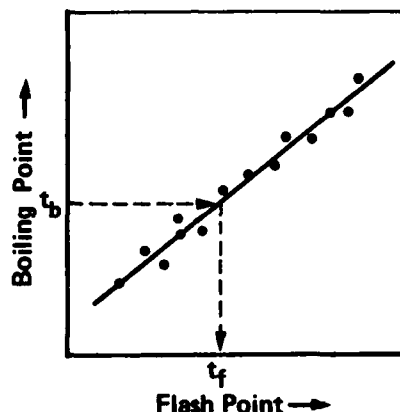


FIGURE 18-4 Graphical Determination of Open- or Closed-Cup Flash Point

18-6 FLASH POINTS OF MIXTURES

It is frequently necessary to estimate the flash point of a mixture of substances. Some references that address this subject are cited below.

Thiele [14] provides a method for estimating flash points for blends of lubricating oils. Butler [5] does the same for middle distillates, claiming that methods given by Nelson [11] and the Factory Mutual Fire Insurance Companies [3] for hydrocarbon fractions are less accurate. In a more recent paper, Hu and Burns [7] address distillate-fuel blends and reference a method by Wickey and Chittenden [19]. Other sources of information on hydrocarbon fractions are Burger [4] and Lenoir [8].

Wu and Finkelman [20] discuss a method for predicting the closed-cup flash points of solvent blends. They cite an earlier method

by Walsham [17] for predicting open-cup flash points. Walsham [18] discusses this topic in a later paper also.

18-7 AVAILABLE DATA

There are a number of compilations of flash-point data that can be useful in applying the approaches of Butler and of others. The following are examples:

Fire Protection Handbook, NFPA [10] — Contains flash point, boiling point, LFL and other data for hundreds of compounds. Flash points are mostly of the closed-cup type.

Fire Protection Guide on Hazardous Materials, NFPA [9] — Contains the same tables as the previous source in a less expensive volume.

CHRIS Hazardous Chemical Data, USCG [16] — Contains individual data sheets for 900 compounds. Items include both closed-cup and open-cup flash points, when available, and boiling points, LFL's, etc. Earlier version for 400 substances also had vapor pressure vs. temperature curves.

Chemical Data Guide, USCG, [15] — Contains flash point, boiling point, LFL and other data for 279 common compounds. Flash points are mostly of the open-cup type.

"Aldrich Catalog Handbook of Fine Chemicals" [2] — Updated frequently, this catalog contains listings for over 9,000 chemicals. Pertinent data include flash points determined by a Setaflash Closed-Cup Tester, and boiling points.

18-8 SYMBOLS USED

C	= number of carbon atoms in the fuel molecule
χ_{st}	= stoichiometric concentration of fuel vapor in air (vol %)
H	= number of hydrogen atoms in the fuel molecule
LEL	= lower explosive limit concentration of fuel in air (vol %)
LFL	= lower flammable limit concentration of fuel in air (vol %)
O	= number of oxygen atoms in the fuel molecule
S	= number of sulfur atoms in the fuel molecule
X	= number of halogen atoms in the fuel molecule
t_f	= flash point temperature
t_b	= normal boiling point temperature

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19

DENSITIES OF VAPORS, LIQUIDS AND SOLIDS

Leslie H. Nelken

19-1 INTRODUCTION

The density of a substance, ρ , is the ratio of its mass to its volume. The property varies not only with molecular weight but also with molecular interaction and structure: for instance, although primary and tertiary butyl alcohol have the same molecular weight, their respective densities at 20°C are 0.8098 and 0.7887 g/mL. In environmental analysis, the primary reason for estimating the density of a substance is to determine whether gases are heavier or lighter than air, or whether liquids and solids will float or sink in water. Specific applications for density include chemical spill models for substances such as oil or toxic gases. In addition, density is often required for the estimation of other chemical properties, such as molar refraction and viscosity.

Units of density express a mass to volume ratio. For liquids the units are g/mL or mol/mL, and for solids, g/cm³. Liquid densities range from 0.6 to 2.9 g/mL, and the range for solids is about 0.97 to 2.7 g/cm³. Vapor densities are in units of g/L or mg/m³; about 0.5 to 3.0 g/L is the typical range for vapor densities at normal temperatures and pressures.

Specific gravity (SG) is a dimensionless parameter derived from density. It is defined as the ratio of the weight of a given volume of substance at a specified temperature to the weight of the same volume of water at a given temperature. In the notation $SG = 0.8076_{20}^{\circ}$, the super-

script refers to the temperature of the substance at the time of measurement, and the subscript is the water temperature. At 4°C, the density of water is 1.0000 g/mL, so the specific gravity of the liquid is identical to the liquid density relative to the density of water at 4°C.

Methods for estimating the density of the vapor, liquid, and solid phases are discussed separately. A brief overview of the recommended methods is given below.

- *Vapor density* (§19-2) is estimated by use of the ideal gas law. This is an easy and sufficiently accurate method at the pressures and temperatures encountered in environmental problems.

- Two methods are recommended to estimate *liquid density*. The first (§19-5) requires the boiling point of the compound and knowledge of the molecular structure. The average error obtained by this method on a group of about 30 compounds was near 3.4%. The second method (§19-6) is more rigorous but slightly more accurate; inputs include the acentric factor (or boiling point in the absence of the acentric factor), the critical temperature, and the critical pressure. With the exception of the acentric factor, these properties may be estimated by methods detailed in Chapters 12 and 13.

- *Solid density* (§19-8) can be estimated by a method based upon fragment constants. Only the structure of the chemical is required for this method. The following atoms and ions are included in this method: H, C, O, N, S, F, Cl, Br, I, Na⁺, K⁺, Rb⁺, F⁻, Cl⁻, Br⁻, and I⁻. The densities of hydrated solids and various hydrogen-bonded solids can also be estimated by this approach.

19-2 VAPOR DENSITY ESTIMATION

Numerous equations of state have been formulated to account for the nonideal behavior of gases at high temperatures and pressures. These equations have been reviewed by Reid *et al.* [14] and Tarakad [17]. However, for the purposes of environmental analysis, where temperatures are in the range of 0-50°C and pressures approximate 1 atmosphere, the ideal gas law provides a simple, accurate estimation method. For the few applications in which the temperature or pressure is outside the normal range, the Redlich-Kwong equation of state [13,14] is an accurate, though more complicated, technique for estimating the vapor density.

The ideal gas law is expressed as:

$$PV = nRT \quad (19-1)$$

where

- P = pressure (atmospheres)
- V = volume (liters)
- n = the number of moles of gas
- R = ideal gas constant (0.082 atm-L/mol-K)
- T = temperature (K)

Density is defined as weight per volume, in this case by n/V (moles/liter) or, preferably, by nM/V (g/liter) where M is the molecular weight. Rearrangement of Eq. 19-1 results in an expression for the vapor density, ρ_v :

$$\rho_v = \frac{PM}{RT} \quad (19-2)$$

Table 19-1 lists the percent error obtained by estimating the vapor density of 15 gases using the ideal gas law. For purposes of comparison, the error obtained by the more complicated Redlich-Kwong method (which requires an estimate of critical temperature and pressure) is also included for some of the compounds. A calculator capable of solving cubic-order equations is helpful, though not necessary.

Basic Steps

- (1) Obtain the molecular weight of the compound, M .
- (2) Assign values to the temperature T (K) and pressure P (atm) for the system of interest. Note that $R = 0.082$ atm-L/mol-K.
- (3) Calculate ρ_v (g/L) using Eq. 19-2.

Example 19-1 Calculate the density of methyl chloride at 0°C and 1 atm, given $M = 50.49$ g/mol.

By Eq. 19-2, $\rho_v = (1)(50.49)/(0.082)(273) = 2.26$ g/L. The vapor density of methyl chloride given in the literature is 2.31 g/L [14], indicating an error of -2.6%.

19-3 AVAILABLE METHODS FOR ESTIMATING LIQUID DENSITY

Most methods for estimating liquid density are based upon the law of corresponding states. According to this law, properties that are dependent upon intermolecular forces are related to the critical properties in the same way for all compounds. Thus, the estimation of density

TABLE 19-1

Accuracy of the Ideal Gas Law and Redlich-Kwong Methods
for Estimation of Vapor Density

	ρ_v (Literature Value, g/L at 0°C) ^a	Percent Deviation of Estimated Value	
		Ideal Gas Law	Redlich- Kwong
Hydrocarbons			
Methane	0.7168	-0.1	+0.3
Ethane	1.357	-1.0	+0.7
Propene	1.937	-2.9	-1.4
Acetylene	1.173	-0.8	0.0
Allene	1.787	+0.1	+2.4
Halogenated Hydrocarbons			
Methyl chloride	2.310	-2.6	-0.8
Ethyl fluoride	2.198	-2.3	-0.8
Bromoacetylene	4.684	0.0	
O-containing Compounds			
Methyl ether	2.091	-1.6	+0.6
Ethylene oxide	1.965	+0.1	-0.4
Carbon dioxide	1.977	-0.5	
Carbon monoxide	1.250	0.0	
N-containing Compounds			
Cyanogen	2.355	-0.4	+1.1
Ammonia	0.7710	-1.3	
Other			
COS	2.721	-1.4	
Absolute Average Error		1.0	0.8

a. Source: Hodgman *et al.* [7]

generally requires a knowledge of certain critical properties — namely, temperature (T_c), pressure (P_c), and sometimes also the compressibility factor (Z_c). Many of the methods developed for estimating liquid density are described and discussed in Refs. 1,2,6,12,14-17,19 and 20.

The method of Kier *et al.* [10] is an exception to the above, in that it relies only upon the molecular structure of a chemical. The method is based on a topological index called the *connectivity function*, χ , which is correlated with liquid density by a regression equation developed for the applicable chemical class. The density of aliphatic hydrocarbons, mono-alcohols, and acids at 20°C can presently be estimated by substituting χ in the appropriate regression equations. The method is not included in this handbook, however, because of the limited number of chemical classes for which it is applicable and the labor involved in calculating χ for a complex molecule.¹

There are approximately twenty methods for estimating liquid density. Table 19-2 summarizes the characteristics of a few of the more common ones. From the equations, it is obvious that the density of a liquid is a function of temperature. It usually decreases as temperature increases, although there are anomalies (the most familiar being that of water between 0° and 4°C). The density of a liquid is also affected by the polarity of the molecule and by molecular interactions. For the majority of estimation methods, accuracy decreases as the polarity of the compound increases. The critical compressibility factor and acentric factor account for some additional deviation from theoretical behavior. Liquid density increases with pressure, but only slightly; for example, a liquid with a density of 0.4 g/mL at 1 atmosphere increases in density by only 0.01 g/mL at 34 atmospheres in an isothermal system [12].

19-4 SELECTION OF APPROPRIATE METHOD FOR LIQUID DENSITY

The two methods described here have been chosen on the basis of ease of use, minimum amount of input data, and accuracy. The method of Grain [3] is a modification of the Goldhammer equation (cited in Ref. 12) and is invaluable because it requires no critical properties, only molecular weight (M), boiling point (T_b), and molar volume (V_b) at the boiling point.² V_b can be estimated from chemical structure. The second method, that of Bhirud [1], requires more input data, namely, the critical temperature and pressure and the acentric factor. These values are

1. A computer program has been developed for calculating χ [5]. Thus, the method of Kier *et al.* could have significant future potential when regression equations for other chemical classes are developed.
2. Estimation methods for T_b , T_c and P_c are described in Chapters 12 and 13 of this book. Reid *et al.* [14] also provides estimation techniques for T_c and P_c ; molar volume can be estimated by the method given in §19-5.

TABLE 19-2

Some Available Methods for Estimating Liquid Density

Method	Formula ^a	Inputs ^b	Applicable Temperature Range ^c	Remarks
Grain [3] ^d (see § 19-5)	$\rho_L = M \rho_{Lb} [3 - 2 (T/T_b)]^n$	M, T_b, V_b	$T < T_b$	Technique available for estimating V_b within 3-4%. [14]
Bhirud [1] ^d (see § 19-6)	$\rho_L = M P_c / R T_e^a + \omega b$	M, T_c, P_c, ω	$T_r < 1.0$	Average absolute error = 0.76% (max 2.23%) for 24 polar and nonpolar compounds [1].
Gunn and Yamada [4]	$\rho_L = M [V_{sc} V_r^{(0)} (1 - \omega \Gamma)]^{-1}$	M, T_b, T_c, P_c	$0.2 \leq T_r \leq 0.99$	Average absolute error = 0.22% (max = 4.90%) for 32 nonpolar and slightly polar compounds. [4]
Yen and Woods [22]	$\rho_L = M \rho_c [1 + \sum_{i=1}^4 K_i (1 - T_r)^{i/3}]$	M, T_b, T_c, P_c, ρ_c	$T_r < 1.0$	Average absolute error = 2.1% for 200 nonpolar and slightly polar compounds. [6]
Guggenheim [12]	$\rho_L = M \rho_c [1 + \frac{7}{4} (1 - T_r)^{1/3} + \frac{3}{4} (1 - T_r)]$	T_c, M, ρ_c	$T_r < 1.0$	Average error = 6%; requires only 1 critical property. [12]
Modified Rackett Eq. [16]	$1/\rho_L = \frac{MRT_c}{P_c} Z_{RA} e^{1 + (1 - T_r)^{2/7}}$	T_c, P_c, M	Wide	Z_{RA} must be determined experimentally. Average absolute error = 0.6% for 100 compounds. [16]

a. See § 19-10 for explanation of symbols. b. Z_c and ρ_c can be estimated. c. T_r = reduced temperature (T/T_c). d. Recommended method.

unlikely to be available in the literature for a compound whose density is not reported. Methods for estimating the first and second parameters are given in Chapters 12 and 13, respectively; the acentric factor, ω , may be estimated by a method described in §19-6 of this chapter.

Table 19-3 compares the accuracy of the above methods. Grain's method is more accurate for each of the five chemical groups, achieving average and maximum errors of 3.1% and 8.6% respectively. Bhirud's method averages a 7.2% error for the compounds sampled, partly because of the estimated value of the acentric factor used in these calculations.

Grain's method [3] has not been tested on a large number of chemicals, but it appears to work quite well for the compounds in the sample group. It differs from the original Goldhammer equation in that the critical temperature is replaced by the term $1.5 T_b$. The critical temperature actually ranges from 1.2 to 1.7 times the boiling point, but the error introduced by the 1.5 approximation is minimal because it is raised to a fractional power (0.25-0.31). Table 19-4 shows the accuracy of Grain's method in comparison with the results of Goldhammer's method. The additional error caused by the approximation averages 3.7% for 11 sample points; the maximum error is 11%.

Bhirud's method [1] estimates the saturated liquid density of polar and nonpolar organic liquids over a wide temperature range.³ The saturated liquid density is measured when the liquid is in equilibrium with the vapor of the pure compound. Since the pressure exerted by the pure vapor is different from atmosphere pressure, it can slightly affect precise measurements of liquid density; however, as indicated earlier, the effect of a change in pressure of even several atmospheres can be ignored for the applications addressed here [12]. Bhirud's method is reported [1] to achieve an overall average error of 0.76% and maximum error of 2.23% for 24 compounds. Table 19-3 indicates, however, that when one of the required parameters (acentric factor) must be estimated, the error increases about tenfold. Should the critical parameters also require estimation, even greater errors can be expected.

19-5 GRAIN'S METHOD (LIQUID DENSITY)

Grain's method [3] is a modification of a density estimation technique derived by Goldhammer, as reviewed by Reid *et al.* [14] and

3. It should be noted that Bhirud's objective was to develop a method just for normal (nonpolar or slightly polar) fluids [1].

TABLE 19-3

Accuracy of Two Methods for Estimating Liquid Density

Chemical	Literature Value (g/mL) at 20°C Unless Indicated ^a	Percent Deviation of Estimated Value	
		Grain	Bhirud
Hydrocarbons			
Naphthalene, 1-methyl	1.0202	-4.5	-10.9
Benzene, 1-isopropyl, 3-methyl	0.8610	-0.2	- 6.1
Cyclopentene	0.7720	+1.1	+ 1.9
2-Hexadecyne	0.7965	+0.8	b
Halogenated Hydrocarbons			
Fluorobenzene	1.0225	+1.9	- 1.2
Hexanoic chloride, 3-methyl	0.967	+0.7	b
Dibromoethylene	2.1792	-5.9	b
2-Butanone, 3-chloro, 3-methyl	1.0083	-0.7	b
Allyl chloride	0.937	-2.3	- 8.8
p-Dichlorobenzene	1.248 (55°C)	+1.1	- 7.8
O-containing Compounds			
3-p-Cymenol	0.990	-4.7	+14.8
Methoxybenzene	0.9961	-2.6	+ 3.5
Isopropyl ether	0.7214	-8.6	+ 6.4
Butanoic acid, ethyl ester	0.8785	+2.5	+ 5.3
Diethyl ketone	0.8138	+5.7	+ 3.0
p-Dioxane	1.0337	+4.0	+ 1.3
Malonic acid, acetyl, diethyl ester	1.0834 (26°C)	+3.5	b
2-Butanone, 3-chloro, 3-methyl	1.0083	-0.7	b
Hexanoic chloride, 3-methyl	0.967	+0.7	b
Tetrahydrofuran	0.889	+3.5	- 0.9
Methyl isobutyl ketone	0.801	+1.2	+ 0.9
Octadecanol	0.812 (59°C)	-1.8	+43.5
N-containing Compounds			
Aniline, N,N-dimethyl	0.9557	-2.1	+ 1.1
Piperidine	0.8606	-0.8	- 2.0
n-Propylamine	0.7173	-4.8	+ 0.7
Propionitrile	0.7818	+1.9	-29.0
Benzonitrile	1.0102 (15°C)	+2.2	- 8.5
Ethylenediamine	0.896	-9.5	- 6.6

(Continued)

TABLE 19-3 (Continued)

Chemical	Literature Value (g/mL) at 20°C Unless Indicated ^a	Percent Deviation of Estimated Value	
		Grain	Bhirud
S-containing Compounds			
Thiophene	1.0649	+3.4	− 0.8
Methylmercaptan	0.866	−4.0	− 1.0

SUMMARY OF ERRORS

	Grain		Bhirud	
	n	%E	n	%E
Absolute Average Error	28	3.1	23	7.2
Hydrocarbons	4	1.6	3	6.3
Halogenated Hydrocarbons	6	2.1	3	5.9
O-containing	12	3.2	9	8.8
N-containing	6	3.5	6	8.0
S-containing	2	3.7	2	0.9

a. Values from Refs. 7 and 14.

b. Critical points not available for these compounds in the literature.

Gambill [2]. The Goldhammer method requires input of the molar density at the normal boiling point (ρ_{Lb}) and is expressed by the following equation:

$$\rho_L = M\rho_{Lb} \left(\frac{1 - T_r}{1 - T_{br}} \right)^n \quad (19-3)$$

where M is the molecular weight, $T_r = T/T_c$ and $T_{br} = T_b/T_c$. The value of the exponent n varies, depending on the chemical class:

	n
Alcohols	0.25
Hydrocarbons	0.29
Other organics	0.31

Grain modified Eq. 19-3 by using the following approximation:

$$T_c \approx \frac{3}{2} T_b \quad (19-4)$$

TABLE 19-4

Percent Difference Obtained by Grain's Equation
Using the Approximation $T_c = 1.5 T_b$

Compound	T_b (K)	T_c (K)	T_c/T_b	Δ		% Difference $\frac{(a-b)}{a} \times 100$
				a	b	
Acetone	329.7	509.1	1.54			
200K				1.23	1.25	- 1.6
273K				1.11	1.12	- 0.9
Isoamyl propionate	433.4	611.4	1.41			
200K				1.375	1.320	4.0
273K				1.277	1.234	3.4
383K				1.099	1.083	1.5
Methane	111.7	190.7	1.71			
95K				1.075	1.105	- 2.8
110K				1.007	1.011	- 0.4
n-Octadecane	589.3	756	1.28			
323K				1.44	1.28	11.1
450K				1.26	1.16	8.0
550K				1.08	1.05	2.8
Dimethyl ether	249	400.1	1.61			
100K				1.30	1.35	- 3.8

a. Goldhammer's equation

$$\Delta = \left(\frac{1 - T/T_c}{1 - T_b/T_c} \right)^{0.38}$$

b. Grain's equation

$$\Delta = [3 - 2 (T/T_b)]^{0.38}$$

(The exponent 0.38 was chosen to represent a worst-case example.)

T_r is then equal to $2T/3T_b$, $T_{br} = \frac{2}{3}T_b$, and Eq. 19-3 becomes:

$$\rho_L = M\rho_{Lb} [3-2(T/T_b)]^n \quad (19-5)$$

The density at the boiling point is easily determined by estimating the inverse property, the molar volume at the boiling point. Methods for doing this are reviewed by Reid *et al.* [14]; the one used here (that of Schroeder) is a simple, additive method applicable to a large number of compounds, with an average error of 3.4%. Table 19-5 lists the incremental values used in this calculation.

TABLE 19-5

Incremental Values for Estimating Molar
Volume, V_b , by Schroeder's Method

V_b is calculated by summing the incremental values for every atom, chemical structure, or bond listed; e.g., cyclopentene (C_5H_8) = 5(C) + 8(H) + 1 (Ring) + 1 (C=C) = 91 $cm^3/g\text{-mol}$.

Molecular Feature	Increment ($cm^3/g\text{-mol}$)	Molecular Feature	Increment ($cm^3/g\text{-mol}$)
Atoms		I	38.5
C	7	S	21
H	7		
N	7	Rings	- 7
O	7		
Br	31.5	Bonds	
Cl	24.5	Single	0
F	10.5	Double	7
		Triple	14

Source: Reid *et al.* [14]

Basic Steps

- (1) Look up the boiling point, T_b (K), and calculate the molecular weight, M , of the chemical. (T_b may be estimated by the methods given in Chapter 12.)
- (2) Calculate V_b from the molecular structure, using Table 19-5. Calculate $\rho_{Lb} = 1/V_b$.
- (3) Assign the appropriate value to n for the chemical class of the compound, as listed above.
- (4) Apply these values to Eq. 19-5 to estimate ρ_L at the desired temperature, T (K).

Example 19-2 Calculate the density of fluorobenzene (C_6H_5F) at $20^\circ C$ (293K), given $M = 96.11$ g/mol and $T_b = 85.1^\circ C$ (358K).

- (1) Determine V_b from Table 19-5:

6 carbons	= 6(7) =	42
5 hydrogens	= 5(7) =	35
1 fluorine	=	10.5
1 ring	=	-7
3 double bonds	= 3(7) =	21
		101.5

$$\rho_{Lb} = 1/101.5 = 9.852 \times 10^{-3} \text{ g/cm}^3$$

- (2) Assign fluorobenzene to the class "other organics."

Therefore, $n = 0.31$

- (3) Substituting into Eq. 19-5,

$$\begin{aligned} \rho_L &= (96.11) (9.852 \times 10^{-3}) [3 - 2 (293/358)]^{0.31} \\ &= 1.04 \text{ g/cm}^3 \end{aligned}$$

Since the literature value is 1.0225, the error is +2%.

19-6 BHIRUD'S METHOD (LIQUID DENSITY)

Bhirud [1] developed this method of liquid density estimation to suit a wide range of chemical compounds over a large temperature span. The equation is based on the law of corresponding states and requires the acentric factor (ω), critical temperature (T_c), and critical pressure (P_c) as inputs. The following equation is written in terms of parameters a and b , which, in turn, are functions of the reduced temperature, T_r :

$$\ln (P_c V / RT) = a + \omega b \quad (19-6)$$

where

$$\begin{aligned} a &= 1.39644 - 24.076T_r + 102.615T_r^2 - 255.719T_r^3 \\ &\quad + 355.805T_r^4 - 256.671T_r^5 + 75.1088T_r^6 \end{aligned} \quad (19-7)$$

$$\begin{aligned} b &= 13.4412 - 135.7437T_r + 533.380T_r^2 - 1091.453T_r^3 \\ &\quad + 1231.43T_r^4 - 728.227T_r^5 + 176.737T_r^6 \end{aligned} \quad (19-8)$$

Rearrangement of Eq. 19-6 and incorporation of molecular weight allows for direct calculation of the liquid density:

$$\rho_L = MP_c / RT e^{a + \omega b} \quad (19-9)$$

In this equation, the gas constant, R , is expressed as 82.04 cm³-atm/mol-K. The acentric factor, ω , is a measure of the sphericity of the molecule and is affected by the molecular weight and the polarity. It can be calculated by Eq. 19-10, which was developed by Edmister (cited in Ref. 14).⁴

$$\omega = \frac{3}{7} \left(\frac{T_{br}}{1 - T_{br}} \right) \log P_c - 1 \quad (19-10)$$

Basic Steps

- (1) Obtain the values of M , T_c , P_c and ω from the literature. If ω cannot be found, obtain the value of T_b . (See Chapters 12 and 13 for estimation of T_b , T_c and P_c . T_c may also be approximated by Eq. 19-4.)
- (2) If ω was not found, estimate it by Eq. 19-10. Note that $T_{br} = T_b/T_c$.
- (3) Calculate $T_r (= T/T_c)$ and evaluate Eqs. 19-7 and 19-8.
- (4) Insert values determined above into Eq. 19-9 and calculate ρ_L .

Example 19-3 Calculate the density of fluorobenzene at 20°C, given $M = 96.11$ g/mol, $T_b = 85.1^\circ\text{C}$ (358.3K), $T_c = 286.95^\circ\text{C}$ (560.1K), $P_c = 44.6$ atm, and $R = 82.04$ cm³-atm/mol-K.

- (1) $T_{br} = 358.3/560.1 = 0.6397$
- (2) $\omega = \left(\frac{3}{7} \right) \left(\frac{0.6397}{1 - 0.6397} \right) (\log 44.6) - 1 = 0.255$
- (3) $T_r = 293/560.1 = 0.5231$
- (4) Input into Eqs. 19-7 and 19-8 yields

$$a = -1.5951$$

$$b = -0.5410$$

4. Although Eq. 19-10 contains neither molecular weight nor polarity *per se*, both of these properties are represented by the reduced boiling point (T_{br}), because it is affected by them.

(5) Substituting the above into Eq. 19-9,

$$\rho_L = \frac{(96.11)(44.6)}{(82.04)(293) e^{-1.5951 + (0.255)(-0.5410)}} \\ = 1.01 \text{ g/mL}$$

This corresponds well with the literature value, 1.0225; the deviation is -1.2%.

19-7 AVAILABLE METHODS FOR ESTIMATING SOLID DENSITY

In molecular crystals, the actual volume (crystal volume) occupied by a molecule consists of the molecular volume in addition to the empty spaces in the crystal. The ratio of molecular volume to crystal volume expresses the "packing coefficient" of the crystal and ranges from 0.65 to 0.77 [9]. Cady (cited in Ref. 8) incorporates these ideas, which were developed by the Russian crystallographer Kitaigorodsky, into a method to estimate solid densities. He calculates the volume of the molecule as the sum of atomic spheres of Van der Waals radii, corrected for the overlap created by covalently bonded atoms. He fit a large number of explosive-type compounds to a linear function relating the packing coefficient to the mole fraction of hydrogen atoms bonded to carbon in the molecule.

Tarver [18] used an empirical approach to solid density in which atomic volumes are added together. He compiled values for 74 molecular groupings, so that the special volume effects of a common molecular group can be considered. Table 19-6 summarizes the errors associated with 173 compounds, primarily explosives. The error is less than 1% for 40% of these compounds. The largest errors are encountered with compounds containing several polar and bulky constituents, and with those whose substituent molar volumes are based upon only a few data points. The major disadvantages of this approach are (1) the large data base required to provide a sufficient number of examples to test the accuracy of the method and (2) the narrow category of compounds to which the method applies.

Nielsen [11] has developed a somewhat similar approach based on 43 fragment constants, which he has tested on various solids and liquids, again predominantly explosives. As shown in Table 19-7, the percentage error is larger than with the method of Tarver. In his paper, Nielsen discusses the effect of steric factors on density measurements and suggests a qualitative method of correcting for these factors.

TABLE 19-6

Percent Error in Calculated Density Using the Method of Tarver

Class	No. of Compounds	Avg. Error (%)	Number of Compounds Within Error Range		
			0-1%	1-2%	2-3%
Solid Aromatic Explosives Containing NO ₂ , OH, CH ₃ and NH ₂	25	1.29	11	9	5
Aliphatic Compounds Containing NO ₂ , OH, F, CO ₂ H, and ONO ₂	75	1.51	35	24	8
Amines, Nitramine, and Heterocyclic Compounds	73	1.68	24	24	18
Overall	173	1.55	70	57	31

Source: Tarver [18]

TABLE 19-7

Absolute Average Error Calculated for
Density Using the Method of Nielsen

Compound Class	No. of Compounds	Average Error (%)
Amines	16	2.0
Hydrocarbons (Aromatic and Acyclic)	28	4.3
Explosives	16	9.7
Miscellaneous (Halogenated, Ethers, Ketones, Alcohols)	22	6.7
Overall	82	5.5

Source: Nielsen [11]

A third method of estimation, that of Immirzi and Perini [9], is recommended here because it was developed from a data base that was not limited to explosive-type compounds but, rather, 500 organic crystalline compounds ranging in molecular weight from 50 to 1000 g/mole. To compensate for the empty space in an organic crystal, which is accomplished in the Cady and Kitaigorodsky methods by the packing coefficient, Immirzi and Perini assign atomic volumes based upon the number of other atoms bonded to the specific atom. Carbon, for instance, may bond to 2, 3, or 4 other atoms, oxygen to 1 or 2, and nitrogen (in this method) to a maximum of 3 and a minimum of 1.

The following restrictions apply to the method of Immirzi and Perini: (1) crystals that have a structural disorder or are not solids at room temperature are excluded; (2) with the exception of water, crystals may not contain molecules of the solvent; (3) only the elements H, C, O, N, S, F, Cl, Br, I, Na, K, and Rb are considered; and (4) cyclic compounds are limited to derivatives of benzene and naphthalene.

Immirzi and Perini analyzed the method errors by selecting a random sample of 53 crystalline organic compounds whose composition was compatible with the data set used for their regression analysis. Table 19-8 lists the chemical formulas of these compounds and the errors in the estimated molecular volumes. The data indicate an average absolute error of 2.0% in the estimates of crystal density. Approximately 40% of the estimates were within 1% of the measured values, and 57% of the estimates were within 2%. The maximum error was +6.9%.

19-8 METHOD OF IMMIRZI AND PERINI

The additivity method of Immirzi and Perini is based upon the following equation:

$$V_s = \sum_i m_i v_i \quad (19-11)$$

where

- V_s = calculated crystal volume for a single molecule ($\text{\AA}^3/\text{molecule}$)
- m_i = relative stoichiometric multiplicities
- v_i = unit volumes of atomic elements (\AA^3)

Values for v_i are listed in Table 19-9 in units of cubic angstroms; these values were selected to minimize the quantity $(V_c - V_s)^2$, where V_c is the experimentally derived crystal volume.

TABLE 19-8

Errors in Estimates of Crystal Volume for 53 Compounds, by Method of Immerzi and Perini

Compound	Experimental Crystal Volume, V_c (nm ³ /molecule)	Deviation of Estimate ^a (%)	Compound	Experimental Crystal Volume, V_c (nm ³ /molecule)	Deviation of Estimate ^a (%)
C ₂₀ H ₁₆ O ₂	0.4400	0.95	C ₆ H ₁₀ O ₇ · H ₂ O	0.2201	0.84
C ₆ H ₆ O ₂ · CON ₂ H ₄	0.2075	4.32	C ₁₇ H ₁₀ N ₂ Cl ₂	0.3750	0.43
C ₂₀ H ₁₂ O ₅ · C ₃ H ₆ O	0.4676	0.11	C ₂₃ H ₃₅ O ₄ N ₅ S	0.6194	1.59
C ₈ H ₂ O ₄ N ₂ · 6H ₂ O	0.3175	1.40	(C ₆ H ₆ Nl) ₂ · C ₆ H ₆ N ₃ O ₆ · ½C ₆ H ₆	0.5159	1.76
C ₆ H ₂ O ₄ F ₂	0.1574	0.99	C ₁₆ H ₁₀ N ₃ O ₃ Cl	0.3540	2.49
C ₆ H ₃ N ₂ O ₅ Cl	0.2068	2.20	C ₂₂ H ₃₁ O ₂ N	0.4697	4.28
C ₆ H ₄ NO ₃ · K ⁺ · ½H ₂ O	0.1859	2.20	C ₂₄ H ₃₁ O ₆ F	0.5714	1.30
C ₅ H ₆ O ₃	0.1295	3.10	C ₆ H ₁₂ N ₂ O ₄ S ₂ · 2HBr · 2H ₂ O	0.3850	0.65
C ₁₇ H ₁₆	0.3190	0.56	C ₆ H ₁₂ Cl ₂	0.3333	2.30
C ₂₁ H ₂₄ O ₂	0.4132	4.78	C ₁₈ H ₂₁ N ₄ O ₂ Cl	0.4361	0.16
C ₁₃ H ₁₂ N ₄ O ₂ · 2C ₁₀ H ₈ O ₂ · 3H ₂ O	0.7533	0.07	C ₂₀ H ₁₄ O ₄	0.4044	0.25
C ₁₀ H ₂₀ N ₂ O ₄ S ₂ · 2HCl	0.4234	0.70	C ₂₀ H ₁₄ U ₄	0.4129	2.31
C ₈ H ₁₅ N ₂ O ₂	0.2442	4.60	C ₇ H ₁₅ NO	0.2151	6.90
C ₈ H ₁₅ NO ₆	0.2536	0.24	C ₉ H ₁₉ NO	0.2629	5.10
C ₆ H ₆ N ₄ O ₂ · HCl · H ₂ O	0.2280	2.19	C ₁₀ H ₂₀ N ₂ O ₃ S ₂	0.3370	0.88
C ₁₈ H ₂₂ O ₂	0.3641	2.64	C ₈ H ₁₅ NO ₇	0.2710	0.00
C ₁₇ H ₂₂ N ₂ O ₃	0.3835	0.75	C ₇ H ₁₃ NO ₂	0.1959	1.40
C ₂₇ H ₄₆	0.5576	6.55	C ₄ H ₁₃ NO ₂ ⁺ · C ₈ H ₁₁ N ₂ O ₃ ⁻	0.3853	5.67
C ₂₉ H ₅₀	0.6141	4.76	C ₄ H ₁₂ NO ⁺ · C ₈ H ₁₁ N ₂ O ₃ ⁻	0.3644	1.65
C ₁₆ H ₂₀ N ₄ O ₆	0.4475	6.48	C ₄ H ₁₂ NS ₂ ⁺ · Br ⁻ · H ₂ O	0.2510	1.54
C ₁₆ H ₂₇ O ₅ N	0.4319	1.51	C ₁₀ H ₁₅ BrO	0.2561	0.22
C ₁₆ H ₁₆ N ₄	0.3334	2.10	C ₁₀ H ₁₄ Br ₂ O	0.2898	2.81
C ₆ H ₁₃ NO ₂	0.1828	0.40	C ₁₄ H ₂₀ NCl	0.3229	2.02
C ₂₁ H ₃₀ O ₂ · C ₆ H ₆ O ₂	0.5906	0.02	C ₁₅ H ₁₀ O ₅	0.2990	3.44
C ₃₀ H ₂₂ O ₂ N ₂ Br ₂	0.6091	0.33	C ₁₅ H ₁₃ O ₂ F	0.3153	2.15
C ₉ H ₁₇ N ₃ O ₄ · ½H ₂ O	0.3021	1.21	C ₂₃ H ₂₉ ClO ₄	0.5333	0.31
C ₁₆ H ₂₂ O ₃ N ₂	0.3954	0.76			
				Avg. absolute error = 2.0	

a. Estimated values included corrections for aromatic and non-aromatic 5- or 6-membered rings and for hydrogen bonds in -CONH₂, -CONH, and -COOH groups.

Sources: Immerzi and Perini [9], based on data from *Acta Crystallogr. Sect. B*, 31 (1975).

TABLE 19-9

Volume Increments (v_i) for Common Elements and Ions^a

Element or Ion	v_i (\AA^3)	Std. Error, σ	No. of Contributors
-H	6.9	0.4	5228
$\begin{matrix} =\text{C}= \\ -\text{C}\equiv \end{matrix}$	15.3	0.7	74
$-\text{C}\leq$	13.7	0.6	453
$>\text{C}<$	11.0	0.9	1165
=O	14.0	0.5	649
-O-	9.2	0.5	468
N \equiv	16.0	1.3	30
N \leq	12.8	0.8	68
N \leq	7.2	0.8	354
S	23.8	0.9	92
-F	12.8	1.5	14
-Cl	26.7	0.5	134
-Br	33.0	0.5	120
-I	45.0	1.3	26
Cl ⁻	28.9	1.5	39
Br ⁻	39.3	1.5	20
I ⁻	56.6	2.5	11
Na ⁺	13.6	2.2	16
K ⁺	27.3	1.6	32
Rb ⁺	34.1	2.2	15
H ₂ O	21.5	0.8	68
Benzene frame (carbons only)	75.2	2.5	443
O-H ··· O hydrogen-bond	- 2.6	0.7	206
N-H ··· O hydrogen-bond	- 2.8	0.5	152
N-H ··· N hydrogen-bond	- 0.3	1.7	11
Non-aromatic rings (rough est.)	- 3.0		
Naphthalene frame (carbons only)	123.7		

^a. Different coordination numbers are considered for C, N, and O.

Source: Immerzi and Perini [9]

Once V_s is determined, it is substituted in Eq. 19-12 to calculate the solid density, ρ_s . In this equation, M is the molecular weight of the compound.

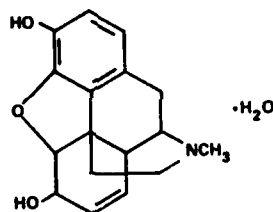
$$\rho_s = \frac{1.660M}{V_s} \quad (19-12)$$

Basic Steps

- (1) Diagram the structure of the chemical, being careful to identify sites of intramolecular hydrogen bonding.
- (2) Find in Table 19-9 the volume increment (v_i) for each atom, ion, or structure in the molecule. Sum these values in proportion to their frequency (m_i) in the molecule, as indicated in Eq. 19-11. The resulting sum is the estimated crystal volume, V_s , in $\text{\AA}^3/\text{molecule}$.
- (3) Obtain the crystal density, ρ_s , in g/cm^3 by substituting V_s and the molecular weight, M , in Eq. 19-12.

Example 19-4 Estimate the crystal density of morphine ($\text{C}_{17}\text{H}_{19}\text{NO}_3 \cdot \text{H}_2\text{O}$). The molecular weight (M) is 303.35 g/mol.

- (1) The structure is:



- (2) The volume increments from Table 19-9 are:

	$m_i (v_i)$
Benzene frame carbons :	1 (75.2)
$>\text{C}<$:	9 (11.0)
$>\text{C} =$:	2 (13.7)
$-\text{H}$:	19 (6.9)
$-\text{O}-$:	3 (9.2)
$\text{N}<$:	1 (7.2)
H_2O :	1 (21.5)

Non-aromatic rings : $\frac{4(-3.0)}{V_s = \sum_i m_i v_i = 377.0 \text{ Å}^3/\text{molecule}}$

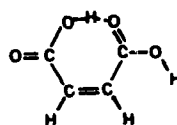
(3) Substituting V_s and M in Eq. 19-12:

$$\rho_s = 1.660 (303.35)/377.0 = 1.336 \text{ g/cm}^3$$

The observed value is 1.317 g/cm^3 [19], indicating an error of +1.4%.

Example 19-5 Estimate the crystal density of maleic acid, *cis*-(COOH)CHCH(COOH). The molecular weight, M , is 116.07 g/mol.

(1) The structure is:



Note the presence of intramolecular hydrogen bonding of the $\text{O-H} \cdots \text{O}$ type.

(2) The volume increments from Table 19-9 are:

	$m_i (v_i)$
$>\text{C} =$: 4 (13.7)
$=\text{O}$: 2 (14.0)
$-\text{O}-$: 2 (9.2)
$-\text{H}$: 4 (6.9)
$\text{O-H} \cdots \text{O}$ hydrogen bond	: $\frac{1(-2.6)}{V_s = \sum_i m_i v_i = 126.2 \text{ Å}^3/\text{molecule}}$

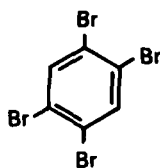
(3) Substituting V_s and M into Eq. 19-12,

$$\rho_s = 1.660 (116.07)/126.2 = 1.527 \text{ g/cm}^3$$

The observed value is 1.590 g/cm^3 ($20^\circ/4^\circ$) [19], indicating an error of -4.0%.

Example 19-6 Estimate the crystal density of 1,2,4,5-tetrabromobenzene, $\text{C}_6\text{H}_2\text{Br}_4$. The molecular weight, M , is 393.74 g/mol.

- (1) The structure is:



- (2) The volume increments from Table 19-9 are:

	$m_i (v_i)$
Benzene frame carbons	: 1 (75.2)
- Br	: 4 (33.0)
- H	: 2 (6.9)
$V_s = \sum_i m_i v_i = 221.0 \text{ \AA}^3/\text{molecule}$	

- (3) Substituting V and M in Eq. 19-12:

$$\rho_s = 1.660 (393.74)/221.0 = 2.958 \text{ g/cm}^3$$

The observed value is 3.072 g/cm^3 ($20^\circ/4^\circ$) [19], indicating an error of -3.7%.

19-9 AVAILABLE DATA

Standard handbooks of chemical properties usually include density. Appendix A lists some general handbooks. For measured or calculated crystal densities, a good source is the following reference, which lists values of 7,500 organic and organo-metallic chemicals:

Donnay, J.D.H. and H.M. Ondik, *Organic Compounds*, Vol. I of *Crystal Data Determinative Tables*, 3rd ed., U.S. Dept. of Commerce, National Bureau of Standards, and the Joint Committee on Powder Diffraction Standards (1972).

Volume II of this series includes principally inorganic compounds, although cyanides and cyanates are also listed.

19-10 SYMBOLS USED

- a = constant in Bhirud's method (Eq. 19-6)
- b = constant in Bhirud's method (Eq. 19-6)
- m_i = relative stoichiometric multiplicities (Eq. 19-11)
- M = molecular weight (g/mol)

n = number of moles in Eq. 19-1; also, coefficient in Eq. 19-3
 P = pressure (atm)
 P_c = critical pressure (atm)
 R = gas constant = $82.04 \text{ cm}^3\text{-atm/mol-K} = 0.082 \text{ L-atm/mol-K}$
 SG = specific gravity
 T = temperature (K)
 T_b = temperature at the boiling point (K)
 $T_{br} = T_b/T_c$
 T_c = critical temperature (K)
 $T_r = T/T_c$
 U = parameter in Eq. 19-6
 V = volume (L)
 V_b = molar volume at the boiling point ($\text{\AA}^3/\text{molecule}$)
 V_c = critical volume (L)
 V_e = experimental crystal volume in Table 19-8
 v_i = atomic volume in Eq. 19-11 (\AA^3)
 V_s = calculated crystal volume of a single molecule in Eq. 19-11 ($\text{\AA}^3/\text{molecule}$)
 V_{sc} = scaling volume (Table 19-2)
 $V_r^{(o)}$ = volume parameter (Table 19-2)
 Z_c = critical-compressibility factor in Table 19-2
 Z_{RA} = parameter in Table 19-2

Greek

ω = Pitzer acentric factor (unitless)
 ρ = density
 ρ_c = critical density (mol/mL)
 ρ_L = liquid density (g/mL)
 ρ_{Lb} = molar density at the boiling point (mol/mL)
 ρ_s = solid density (g/cm³)
 ρ_v = vapor density (g/L)
 χ = connectivity function

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20

SURFACE TENSION

Clark F. Grain

20-1 INTRODUCTION

Surface tension affects the extent of spreading when a liquid chemical is spilled on land or water. It is also important with respect to the emulsification of liquids that are mixed with water and in their adsorption on solid surfaces.

The molecules at the surface of a liquid are subjected to unequal forces. In general, we consider only the interface between the surface of the liquid and a reference gas (air or the vapor of the liquid). If the density of the gas or vapor is low, the molecules at the liquid surface are attracted toward the bulk liquid; the gas or vapor phase exerts considerably less attraction. As a result, the surface is in *tension*, which causes it to contract to a minimum area consistent with the mass of material and the container walls. This force is a characteristic property of a given liquid at a given temperature.

The surface tension is defined as the force per unit length (usually dynes/cm) in the plane of the surface and is represented by the symbol σ . It may also be expressed as energy per unit area (ergs/cm²). Surface tensions for most organic liquids are between 25 and 40 dynes/cm at room temperature, although polyhydric alcohols range up to 65 dynes/cm. For comparison, the surface tension of water at 25°C is 72 dynes/cm.

The two methods for estimating σ that are recommended in this chapter require, as inputs, the parachor, density (or molar volume), boiling point, and values of characteristic constants. Method 1 requires only the parachor and measured density values; more parameters are needed with method 2, but all of them can be estimated.

By either method, errors typically average 5%, but individual values can deviate as much as 30% from measured values.

20-2 AVAILABLE METHODS

The most general estimation method is that of MacLeod and Sugden. MacLeod [5] suggested an empirical relationship between surface tension and liquid density. Sugden [9] later showed that the empirical constant appearing in MacLeod's formulation was identical to a constitutive constant called the parachor. The equation introduced by Sugden is:

$$\sigma^{1/4} = P \frac{(\rho_L - \rho_v)}{M} \quad (20-1)$$

where

- σ = surface tension (dynes/cm)
- P = parachor
- ρ_L = liquid density (g/cm³)
- ρ_v = vapor density (g/cm³)
- M = molecular weight (g/mol)

The parachor can be visualized as a comparative volume between two liquids and is reasonably independent of temperature. Quayle [7] presented a comprehensive review of methods for estimating the parachor and devised one that is suitable for a wide variety of organic compounds.

Equation 20-2, a more familiar form of Eq. 20-1, can be used to calculate σ if the temperature dependency of ρ_L and ρ_v are known.

$$\sigma = \left[P \frac{(\rho_L - \rho_v)}{M} \right]^4 \quad (20-2)$$

For most purposes ρ_v is so much smaller than ρ_L that it can be ignored.

Equation 20-2 then becomes

$$\sigma = \left(\frac{P \rho_L}{M} \right)^4 \quad (20-3)$$

Equation 20-3 is the basic equation for method 1. In method 2 the equation is altered to permit calculation of surface tension when a measured value of ρ_L is unavailable. One of the methods discussed in Chapter 19 is used to estimate ρ_L . Details of the derivation are given in §20-4.

Several other methods are available that use as inputs experimental or estimated values of the heat of vaporization, viscosity, critical temperature, and critical pressure. These have been reviewed by Gambill [1,2] and Reid *et al.* [8]. Table 20-1 lists a representative sample of available methods and comments on their applicability.

The surface tension of mixtures of organic liquids can be treated, in a first approximation, as a linear function of the mole fractions of the pure components. The estimates obtained are very approximate; further refinements are necessary for more accurate estimates. The available methods for these mixtures are discussed by Reid *et al.* [8].

Mixtures of organic liquids and water are even more complicated, and the methods for mixtures of organic liquids only cannot be used. Discussions of methods for obtaining the mixture surface tension of organic liquids and water are given in Chapter 21 and in Ref. 8.

Methods 1 and 2 were chosen because of their generality: they can be applied to a wide variety of materials, including polar and associated organic liquids. The other methods are restricted to hydrocarbon and polar (but nonassociated) liquids.

20-3 METHOD 1 (MacLEOD-SUGDEN)

If measured liquid densities are available as a function of temperature, Eq. 20-3 provides a quite simple and surprisingly accurate method for estimating surface tension. Parachor values are estimated from the table devised by Quayle [7], which is reproduced here as Table 20-2.

Reid *et al.* [8] tested Eq. 20-3 for 28 compounds, including alcohols. They found an average error of 4.5% and a maximum error of -20% (Table 20-3).

TABLE 20-1
Some Methods for Estimating Liquid Surface Tension

Method	Formula ^b	Inputs ^b	Range (dynes/cm)	Comments
Macleod-Sugden [5,9] ^a	$\sigma = (P\rho_L/M)^{1/3}$	P, ρ_L, M	15-65	P can be estimated; measured ρ_L must be available; versatile. Average error ~5%.
Grain ^a	$\sigma = [P(1+k)/V_b \cdot (3-2T/T_b)^n]^{1/4}$	P, n, k, T_b, V_b	15-65	All inputs can be estimated; versatile. Average error ~5%.
Walden [10]	$\sigma = \Delta H_{vb}/3.64V_b$	$\Delta H_{vb}, V_b$	20-40	Inputs can be estimated; hydrocarbons only. Average error ~5%.
Mayer [4]	$\sigma = \frac{(1-A) \Delta H_v}{(36\pi \cdot N_L \cdot V^2)^{1/3}}$	$A, \Delta H_v, N_L, V$	20-40	$N_L = 2.687 \times 10^{19}/\text{cm}^3$; other parameters can be estimated; not applicable to alcohols. Average error ~4%.

a. Recommended method.

b. See §20-5 for explanation of symbols.

TABLE 20-2

Parachor Increments

Group	Increment	Group	Increment
CH ₂ in -(CH ₂) _n		Single bond	0.0
n < 12	40.0	Semipolar bond	0.0
n > 12	40.3	Triple bond	40.6
C	9.0	Carbonyl bond in ketones:	
H	15.5	R + R' = 2	22.3
in OH	10.0	3	20.0
in HN ^a	12.5	4	18.5
O	19.8	5	17.3
O ₂ in esters	54.8	6	17.3
N	17.5	7	15.1
S	49.1	8	14.1
P	40.5	9	13.0
F	26.1	10	12.6
Cl	55.2	Alkyl groups	
Br	68.0	1-Methylethyl	133.3
I	90.3	1-Methylpropyl	171.9
Se	63	1-Methylbutyl	211.7
Si	31	2-Methylpropyl	173.3
Al	55	1-Ethylpropyl	209.5
Sn	64.5	1,1-Dimethylethyl	170.4
As	54	1,1-Dimethylpropyl	207.5
Singlet linkage ^b	-9.5	1,2-Dimethylpropyl	207.9
Hydrogen bridge	-14.4	1,1,2-Trimethylpropyl	243.5
Ethylenic bond		Position differences in benzene: ^c	
Terminal	19.1	Ortho-meta	1.8-3.4
2,3-Position	17.7	Meta-para	0.2-0.5
3,4-Position	16.3	Ortho-para	2.0-3.8
Chain branching, per branch	-3.7	Ring size	
Secondary-secondary adjacency	-1.6	3-membered ring	12.5
Secondary-tertiary adjacency	-2.0	4-membered ring	6.0
Tertiary-tertiary adjacency	-4.5	5-membered ring	3.0
		6-membered ring	0.8
		7-membered ring	4.0

a. For second H in primary amines use increment of 15.5.

b. Bond containing an unpaired electron.

c. Small differences are seen in the Parachor values of di-substituted benzenes. Ortho compounds have the smallest values followed, in turn, by meta and para compounds. The "increments" given are the range of differences noted for the indicated compound pairs.

Source: Quayle [7].

TABLE 20-3

Error in Estimating Surface Tension of Pure Liquids by
Macleod-Sugden Method

Compound	t (°C)	Measured	Error (%)
		σ (dynes/cm)	
Acetic acid	20	27.59	-4.6
	60	23.62	-3.2
Acetone	25	24.02	-5.4
	35	22.34	-3.9
	45	21.22	-4.5
Aniline	20	42.67	-3.2
	40	40.50	-6.0
	60	38.33	-7.1
	80	36.15	-8.8
Benzene	20	28.88	-5.1
	40	26.25	-5.6
	60	23.67	-5.0
	80	21.20	-3.9
Benzonitrile	20	39.37	-2.0
	50	35.89	-3.4
	90	31.26	-4.2
Bromobenzene	20	35.82	-0.7
	50	32.34	-1.4
	100	26.54	-0.7
<i>n</i> -Butane	-70	23.31	11
	-40	19.69	5.2
	20	12.46	1.5
Carbon disulfide	20	32.32	3.8
	40	29.35	3.8
Carbon tetrachloride	15	27.65	-1.1
	35	25.21	-1.2
	55	22.76	-1.0
	75	20.31	0.1
	95	17.86	2.5
Chlorobenzene	20	33.59	-0.6
	50	30.01	0.7
	100	24.06	5.8
<i>p</i> -Cresol	40	34.88	0.5
	100	29.32	-0.3

(continued)

TABLE 20-3 (Continued)

Compound	t (°C)	Measured σ (dynes/cm)	Error (%)
Cyclohexane	20	25.24	-3.9
	40	22.87	-3.5
	60	20.49	-2.2
Cyclopentane	20	22.61	-5.6
	40	19.68	-2.4
Diethyl ether	15	17.56	0
	30	16.20	0.4
2,3-Dimethylbutane	20	17.38	-0.9
	40	15.38	0.6
Ethyl acetate	20	23.97	-4.6
	40	21.65	-4.8
	60	19.32	-4.3
	80	17.00	-2.7
	100	14.68	0.5
Ethyl benzoate	20	35.04	-1.9
	40	32.92	-2.7
	60	30.81	-3.1
Ethyl bromide	10	25.36	-5.3
	30	23.04	-6.1
Ethyl mercaptan	15	23.87	-6.7
	30	22.68	-9.1
Formamide	25	57.02	-8.8
	65	53.66	-15
	100	50.71	-20
<i>n</i> -Heptane	20	20.14	-0.6
	40	18.18	0.7
	60	16.22	3.1
	80	14.26	6.8
Isobutyric acid	20	25.04	1.2
	40	23.20	0.5
	60	21.36	-1.2
	90	18.60	-3.5
Methyl formate	20	24.62	-7.6
	50	20.05	-7.2
	100	12.90	-7.4
	150	6.30	-8.8

(continued)

TABLE 20-3 (Continued)

Compound	t (°C)	Measured σ (dynes/cm)	Error (%)
Methyl alcohol	20	22.56	-13
	40	20.96	-15
	60	19.41	-17
Phenol	40	39.27	-6.7
	60	37.13	-7.3
	100	32.86	-7.8
<i>n</i> -Propyl alcohol	20	23.71	-0.6
	40	22.15	-1.9
	60	20.60	-3.3
	90	18.27	-4.0
<i>n</i> -Propyl benzene	20	29.98	0.2
	40	26.83	0.8
	60	24.68	2.1
	80	22.53	3.9
	100	20.38	6.6
Pyridine	20	37.21	-2.8
	40	34.60	-3.6
	60	31.98	-4.1

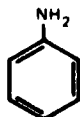
Source: Reid, Prausnitz, and Sherwood [8].

Basic Steps

- (1) Draw the structure of the compound.
- (2) Estimate the parachor (*P*) using Table 20-2. Sum the atomic, group, and structural fragment constants in this table in direct proportion to their occurrence in the molecule.
- (3) Obtain the measured density of the liquid, ρ_L , from the literature. (See §20-6.)
- (4) Insert the above values along with the molecular weight into Eq. 20-3 and calculate the surface tension, σ , in dynes/cm.

Example 20-1 Calculate the surface tension of aniline, $C_6H_5NH_2$, at 20°C. The measured value of σ is 42.7 dynes/cm [8].

- (1) The structure is



(2) From Table 20-2,

$$\begin{aligned}
 1N &= 1 \times 17.5 &= 17.5 \\
 H \text{ in } HN &= 1 \times 12.5 &= 12.5 \\
 6H &= 6 \times 15.5 &= 93.0 \\
 6C &= 6 \times 9.0 &= 54.0 \\
 \text{Dbl. bond} &= 3 \times 19.1 &= 57.3 \\
 \text{Ring closure (6-membered)} &= 0.8 \\
 P &= 235.1
 \end{aligned}$$

(3) From the literature (CRC handbook [11]):

$$\begin{aligned}
 \rho_L &= 1.022 \text{ g/cm}^3 \text{ at } 20^\circ\text{C} \\
 M &= 93.12 \text{ g/mole}
 \end{aligned}$$

(4) Substituting in Eq. 20-3,

$$\begin{aligned}
 \sigma &= \left(\frac{235.1 \times 1.022}{93.12} \right)^4 \\
 &= (2.580)^4 \\
 &= 44.3 \text{ dynes/cm, which deviates } + 3.7\% \text{ from the measured value.}^1
 \end{aligned}$$

Example 20-2 Estimate the surface tension of ethyl acetate. (Measured $\sigma = 24.0$ dynes/cm at 20°C [8].)

(1) The structure is $\text{CH}_3\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{CH}_2\text{CH}_3$

(2) From Table 20-2,

$$\begin{aligned}
 4C &= 4 \times 9.0 &= 36.0 \\
 8H &= 8 \times 15.5 &= 124.0 \\
 \text{O}_2 \text{ in ester} &= 54.8 \\
 P &= 214.8
 \end{aligned}$$

(3) From the literature (CRC handbook [11]):

$$\begin{aligned}
 \rho_L &= 0.901 \text{ g/cm}^3 \text{ at } 20^\circ\text{C} \\
 M &= 88.1 \text{ g}
 \end{aligned}$$

(4) Substituting in Eq. 20-3,

$$\sigma = \left(\frac{214.8 \times 0.901}{88.1} \right)^4$$

1. Table 20-3 shows a different estimated value by Reid *et al.* [9]; the difference in estimated values is presumably due to different assumptions on the use of the parachor increments and/or a different density value.

$$= (2.1 \times 10^{-7})^4$$

$$= 23.3 \text{ dynes/cm}$$

The deviation from the measured value is -2.9%. (See footnote 1, p. 20-9)

20-4 METHOD 2 (GRAIN)

If the density of the liquid is unknown, one of the methods presented in Chapter 19 may be used. The one shown in Eq. 20-4 is particularly useful. (Details are given in §19-4.)

$$\rho_L = \rho_{Lb} (3 - 2 T/T_b)^n \quad (20-4)$$

where

$$\begin{aligned} \rho_{Lb} &= \text{liquid density at } T_b \text{ (g/cm}^3\text{)} \\ T_b &= \text{boiling point (K)} \\ n &= \text{constant for class of compound} \end{aligned}$$

The density at T_b can be estimated from the molar volume, V_b , using the additive schemes of either Schroeder (in Ref. 6) or LeBas [3]. The volume increments for these methods were listed earlier in Tables 19-4 and 12-12 respectively.

Substitution of Eq. 20-4 into Eq. 20-3 and replacement of ρ_{Lb} with its equivalent, M/V_b , yields the following:

$$\sigma = \left[\frac{P}{V_b} (3 - 2 T/T_b)^n \right]^4 \quad (20-5)$$

Values of n for various classes of compounds are shown in Table 20-4.

When applied to primary amines and amides, Eq. 20-5 severely underestimates the surface tension if V_b is calculated by the Schroeder method. The use of LeBas volumes, on the other hand, leads to overestimates for these compounds if they contain less than six carbon atoms. A weighted average value of V_b from both methods could be used; however, the values of the LeBas volumes approach those obtained by the Schroeder method as the number of carbon atoms increases, so the surface tension would still be underestimated. The degree of underestimation is even greater for diols and triols but considerably less for alcohols and phenols. The surface tension of completely halogenated hydrocarbons, in contrast, tends to be overestimated.

TABLE 20-4

Values of Constants k and n

Compound Class	k	n
Alcohols and Phenols	0.020	0.25
Amides	0.065	0.25
Amines (primary)	0.065	0.25
Amines (secondary and tertiary)	0	0.25
Completely Halogenated Hydrocarbons	-0.028	0.29
Diols, Triols	0.10	0.25
Hydrocarbons	0	0.29
All Other Compounds	0	0.31

Sources:

k: Calculated, by the author, from experimental data on one member of the homologous series. The same value of k can be used on other members of the series.

n: Reid, Prausnitz and Sherwood [8] for "alcohols", "hydrocarbons", and "all other compounds"; values for other compound classes contributed by the author of this chapter.

The obvious solution is to modify the value of V_b to suit the class of compound. This is accomplished by Eq. 20-6, where the value of k is chosen from those listed in Table 20-4.

$$V'_b = V_b / (1+k) \quad (20-6)$$

Incorporation of the correction factor in Eq. 20-5 yields the following:

$$\sigma = \left[\frac{P(1+k)}{V_b} (3-2 T/T_b)^n \right]^4 \quad (20-7)$$

Equation 20-7 can be applied to a wide variety of liquids. However, difficulties may be encountered with perhalogenated compounds such as tetrafluorodichloroethane: a k factor can be estimated, but it will not be applicable to all perhalogenated materials. Surface tensions estimated from Eq. 20-7 are compared with measured values for 32 common organic compounds in Table 20-5.

To determine how well Eq. 20-7 accounts for the influence of temperature, the surface tensions of three compounds were estimated for various temperatures and compared with measured values (Table 20-6). Except

TABLE 20-5

Comparison of Measured Surface Tensions with
Values Calculated by Method 2

Compound	t (°C)	Surface Tension (dynes/cm)		Error (%)
		Measured ^a	Estimated	
Acetamide	85	39.0	39.1	0.3
Acetic acid	20	27.6	29.1	5.4
Acetone	25	24.0	24.0	0
Acetonitrile	56	29.1	31.0	6.5
Aniline	20	42.7	42.9	+0.9
Benzaldehyde	30	37.4	39.9	6.7
Benzamide	130	38.1	40.4	6.0
Benzene	20	28.8	27.0	-6.3
Benzonitrile	20	39.4	42.9	8.9
Benzylamine	20	39.1	38.7	-0.1
Bromobenzene	20	35.8	34.3	4.1
<i>n</i> -Butane	-40	19.7	19.4	-1.5
Carbon disulfide	20	32.3	34.3	6.2
Carbon tetrachloride	35	25.2	25.9	2.8
Chlorobenzene	20	33.6	34.9	3.9
Diethylamine	25	16.3	15.7	-3.9
Ethyl acetate	20	24.0	25.0	4.2
Ethyl alcohol	20	22.4	23.9	6.7
Ethylamine	25	19.2	18.3	-4.7
Formamide	0	59.6	55.1	-7.6
Glycerol	20	63.4	64.8	2.2
Heptaidehyde	20	26.6	29.2	9.7
Heptane	20	20.1	20.9	4.0
2-Hexanol	25	24.3	25.5	4.9
Methanol	20	22.6	23.3	3.0
Methylamine	-20	23.0	22.6	-1.7
Phenol	40	39.3	35.8	-8.9
<i>n</i> -Propyl alcohol	20	23.7	24.6	3.8
Propylamine	19	22.0	22.2	0.9
Tetrachlorodifluoroethane	30	22.7	28.7	25.9
Tetrachloroethylene	20	31.7	31.8	+0.3
Trimethylamine	-32	20.0	21.0	5.0
Average error				= 5.1%
Maximum error				= 25.9%

a. From Quayle [7] and Reid, Prausnitz and Sherwood [8].

TABLE 20-6

Temperature Dependence of Measured and Calculated Surface Tensions

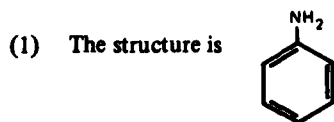
Compound	t (°C)	σ_t (dynes/cm)		Error (%)
		Measured	Calculated	
Acetone	25	24.0	24.0	0
	35	22.3	22.5	0.8
	45	21.2	21.0	-0.9
	56.6 (t_b)	19.5	19.3	-1.0
Glycerol	20	63.4	64.8	2.2
	90	58.6	56.6	-3.4
	150	51.9	49.5	-4.6
	291 (t_b)	40.0	33.1	-17.3
Carbon tetrachloride	15	27.7	29.1	5.0
	35	25.2	25.9	2.8
	55	22.8	23.5	3.1
	75	20.3	20.7	2.0
	95	17.9	18.0	0.6

for glycerol, the correlation is satisfactory for temperatures up to the normal boiling point; even with glycerol, reasonable results are obtained over at least a range of 100°C. This equation is not recommended if T is above the normal boiling temperature.

Basic Steps

- (1) Draw the structure of the compound.
- (2) Calculate the parachor (P) as in method 1.
- (3) Estimate the molar volume (V_b) using Table 19-5 or 12-12 (Schroeder method, Table 19-5, preferred).
- (4) Obtain k and n from Table 20-4.
- (5) Obtain the boiling point, T_b (K), from the literature (see Appendix A) or estimate via one of the methods in Chapter 12.
- (6) Calculate T/T_b . (T = system temperature in K.)
- (7) Substitute these values in Eq. 20-7 and calculate the surface tension, σ , in dynes/cm.

Example 20-3 Calculate the surface tension of aniline at 20°C. (The measured value [8] is 42.7 dynes/cm.)



(2) From Table 20-2, $P = 235.1$ (see Example 20-1).

(3) Determine V_b from Table 19-4:

$$\begin{aligned} 6C &= 6(7) &= 42 \\ 7H &= 7(7) &= 49 \\ 1N & &= 7 \\ 1 \text{ 6-membered ring} & &= -7 \\ 3 \text{ double bonds} &= 3(7) &= 21 \\ V_b &= 112 \text{ cm}^3/\text{mol} \end{aligned}$$

(4) From Table 20-4,

$$\begin{aligned} k &= 0.065 \\ n &= 0.25 \end{aligned}$$

(5) From the literature,

$$T_b = 457\text{K}$$

(6) $T/T_b = (20+273)/457 = 0.641$

(7) Substitute the above values in Eq. 20-7:

$$\begin{aligned} \sigma &= \left\{ \frac{235.1(1+0.065)}{112} \times [3-(2 \times 0.641)]^{0.25} \right\}^4 \\ &= (2.559)^4 \\ &= 42.9 \text{ dynes/cm, which deviates } +0.5\% \text{ from the measured value.} \end{aligned}$$

Example 20-4 Estimate the surface tension of ethyl acetate at 20°C. (Measured $\sigma = 24.0$ dynes/cm [8].)



(2) From Table 20-2,

$$P = 214.8 \text{ (see Example 20-2).}$$

(3) Determine V_b from Table 19-4:

$$\begin{aligned} 4C &= 4(7) &= 28 \\ 8H &= 8(7) &= 56 \end{aligned}$$

$$\begin{aligned}
 2O &= 2(7) &= 14 \\
 1 \text{ double bond} &= &7 \\
 V_b &= 105 \text{ cm}^3/\text{mol}
 \end{aligned}$$

(4) From Table 20-4,

$$\begin{aligned}
 k &= 0 \\
 n &= 0.31
 \end{aligned}$$

(5) From the literature,

$$T_b = 350\text{K}$$

$$(6) \quad T/T_b = 293/350 = 0.837$$

(7) Substituting in Eq. 20-7:

$$\begin{aligned}
 \sigma &= \left\{ \frac{214.8 (1+0)}{105} [3 - (2 \times 0.837)]^{0.31} \right\}^4 \\
 &= (2.233)^4 \\
 &= 24.9 \text{ dynes/cm, which deviates } +3.8\% \text{ from the measured value.}
 \end{aligned}$$

20-5 SYMBOLS USED

A	= constant in equation for Mayer's method (Table 20-1) = 0.43 at 25°C
ΔH_v	= heat of vaporization (cal/mol)
k	= constant in Eq. 20-7
M	= molecular weight (g/mol)
N_L	= Loschmidt's number ($2.687 \times 10^{19}/\text{cm}^3$) in equation for Mayer's method (Table 20-1)
n	= constant in Eq. 20-7
P	= parachor
T	= temperature (K)
T_b	= normal boiling temperature (K)
t	= temperature (°C)
V	= molar volume (cm ³ /mol)
V_b	= molar volume at the normal boiling temperature (cm ³ /mol)
V'_b	= adjusted molar volume at the normal boiling temperature in Eq. 20-6 (cm ³ /mol)

Greek

ρ_L	= liquid density (g/cm ³)
ρ_v	= vapor density (g/cm ³)
σ	= surface tension (dynes/cm)

Subscripts

b	= boiling point
v	= vapor, vaporization

20-6 AVAILABLE DATA

Surface tension data can be obtained from the general compilations listed in Appendix A. Data on many materials are also available in Refs. 7 and 8.

20-7 REFERENCES

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21

INTERFACIAL TENSION WITH WATER

Clark F. Grain

21-1 INTRODUCTION

The interfacial tension between an organic liquid and water affects such processes as the formation of stable emulsions, the resistance to flow through orifices, and the dispersion of droplets. A measured or estimated value of the interfacial tension may be important when one attempts to determine the fate of a chemical of environmental concern or desires to remove a hazardous liquid from an aqueous environment. For example, in liquid-liquid extraction processes a solvent with a high interfacial tension is required to obtain good phase separation after mixing.

When two immiscible or partially miscible liquids are brought into contact, the interface thus formed possesses free surface energy. This surface energy is numerically equal to the interfacial tension. The magnitude of the interfacial tension is less than the larger of the surface tension values for the pure liquids, because the mutual attraction of unlike molecules at the interface reduces the large unbalance of forces present.

The units commonly used to express interfacial tension are the same as for surface tension, namely, dynes/cm. Interfacial tensions of organic

liquids with water range from zero (for completely miscible liquids) up to the surface tension of water, which is 72 dynes/cm at 25°C.

21-2 AVAILABLE METHODS

Table 21-1 summarizes some basic information on two recommended methods for estimating this property. Method 1 requires as input information the mutual solubilities of the organic liquid and water. Method 2 requires the mutual solubility data and also the surface tensions of the pure components. The surface tension of pure water is well documented over an extensive temperature range; values of this parameter are provided in Table 21-4. The other input data can be obtained from the literature or estimated using the methods outlined in this handbook.

TABLE 21-1

Overview of Recommended Estimation Methods

Method	Information Required ^a	Average Error ^b
1 — Donahue and Bartell [2]	X_o, X_w	15.4%
2 — Antonov [1]	$X_o^w, X_w^w,$ $\sigma_o, \sigma_w,$ V_o, V_w	11.8%

a. X_o = solubility of organic phase in water (mole fraction); X_w = solubility of water in organic phase (mole fraction); X_o^w = mole fraction of organic in water = X_o ; X_w^w = mole fraction of water remaining in water phase = $1 - X_o^w \neq X_w$; σ = surface tension of organic (o) and water (w); V = molar volume of organic (o) and water (w).

b. From Table 21-2.

Method 1 has an average error of 15.4% and a maximum error of 48.5%; method 2 has an average error of 11.8% and a maximum error of 38.6%.

Method 1, the simplest method, is based on a correlation first introduced by Donahue and Bartell [3]. These authors observed a linear relationship between the logarithm of the sum of the solubilities of a mutually saturated liquid with water and the interfacial tension which

exists when these phases are in contact. Their correlation can be expressed analytically as

$$\sigma_{ow} = a - b \ln (X_o + X_w) \quad (21-1)$$

where

- σ_{ow} = interfacial tension (dynes/cm)
- a = -3.33
- b = 7.21
- X_o = mole fraction of organic phase in water
- X_w = mole fraction of water in organic phase

The correlation is strictly valid at 25°C only. However, for moderate departures from this temperature (and if solubility data are available), Eq. 21-1 should be reasonably valid without revised values of a and b .

The second method is based upon an empirical correlation reported by Antonov [1] and known as Antonov's rule:

$$\sigma_{ow} = \left| \sigma_{os} - \sigma_{ws} \right| \quad (21-2)$$

where σ_{os} and σ_{ws} are the mixture surface tensions of the mutually saturated water and organic phases, respectively. In general, the surface tensions of pure components should not be used. A method of estimating the saturated phase surface tension is described in § 21-4.

Equation 21-2 has been criticized by Donahue and Bartell [3] and by Good [7]. However, it is generally applicable and reasonably accurate as long as saturated phase surface tensions are used.

The estimation method with the strongest theoretical base has been described by Girifolco and Good [6] and, more recently, by Good [7]. It is based upon some of the ideas put forth in Hildebrand's [8] treatment of the solubility of nonelectrolytes and the Berthelot [2] "geometric mean" hypothesis for the attractive constant in the Van der Waals equation. The method is expressed by the following equation:

$$\sigma_{ow} = \sigma_o + \sigma_w - 2\phi \sqrt{\sigma_o \cdot \sigma_w} \quad (21-3)$$

where the parameter ϕ is related to the similarity of the cohesive forces across the liquid interface. Values of ϕ approaching or exceeding 1 suggest similar forces, and values less than 1 suggest increasingly disparate forces.

Equation 21-3 was originally proposed for estimating interfacial tensions using pure component surface tensions only. Unfortunately, reliable values of ϕ have been calculated only for hydrocarbon-water systems; when applied to hydrogen-bonded systems such as alcohol-water, calculated values of ϕ do not give acceptably accurate results. Even when the effect of mutual solubility is taken into account, errors in the estimated interfacial tension are too high. Therefore, the method of Eq. 21-3 is not recommended despite its sound theoretical base, and the rest of this chapter will be devoted to the two methods described earlier.

Further information with respect to calculating and/or estimating interfacial tension is given in reviews by Fowkes [4] and Gambill [5].

21-3 METHOD 1

If experimental mutual solubility data are available, Eq. 21-1 represents the simplest and fastest method for estimating interfacial tension. The same calculation can be done graphically with Figure 21-1 if desired. Table 21-2 lists the results obtained with 19 systems representing a diverse group of chemical classes.

Every effort should be made to obtain reliable solubility data. If no experimental values are available, the methods of Chapters 2, 3, and 11 can be used to estimate them.

Basic Steps

- (1) Obtain the mutual solubilities, in mole fraction, of the organic phase in water (X_o) and of water in the organic phase (X_w). If experimental data are not available, the methods of Chapters 2, 3, and 11 may be used to obtain an estimate.
- (2) Calculate $\ln (X_o + X_w)$.
- (3) Calculate the interfacial tension (σ_{ow}) by Eq. 21-1, or read off the value from Fig. 21-1. The result is in dynes/cm.

Example 21-1 Estimate the interfacial tension of the system methyl ethyl ketone (MEK) and water at 25°C.

- (1) From Table 21-2, the solubility of MEK in water at 25°C is 5.6×10^{-2} mole fraction. The solubility of water in MEK at 25°C is 0.35 mole fraction.
- (2) $X_o + X_w = 0.056 + 0.35 = 0.41$
 $\ln (X_o + X_w) = \ln (0.41) = -0.89$

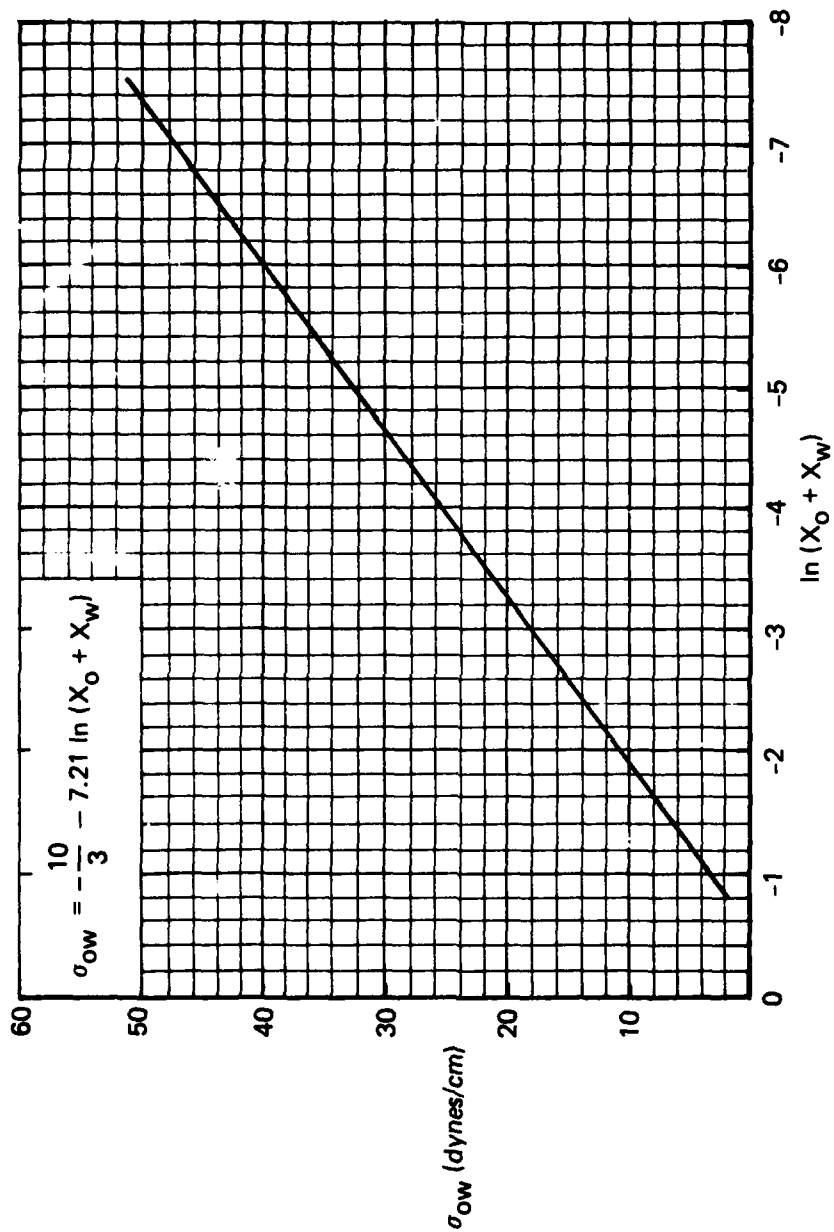


FIGURE 21-1 Graphical Estimation of Interfacial Tension (Method 1)

TABLE 21-2
Estimated vs Experimental Interfacial Tensions with Water

Compound	Temperature (°C)	Solubility (mole fraction)		σ_o (dynes/ cm)	Calculated σ_{ow}		Experimental σ_{ow}
		X_o	X_w		Method 1	Method 2	
Aniline	20	7.3×10^{-3}	2.2×10^{-1}	42.9	7.5	3.7	5.8
Benzene	25	4.9×10^{-4}	4.4×10^{-3}	28.9	34.6	34.0	33.9
Bromobenzene	25	5.3×10^{-5}	2.9×10^{-3}	35.2	38.4	36.5	36.5
<i>n</i> -Butanol	25	1.7×10^{-2}	5.0×10^{-1}	25.1	1.4	2.3	1.9
Butyl acetate	20	1.0×10^{-3}	7.5×10^{-2}	25.2	15.2	8.9	14.5
Carbon tetrachloride	20	9.1×10^{-5}	8.3×10^{-4}	26.2	47.1	46.3	45.0
Cyclohexanol	25	5.0×10^{-3}	4.1×10^{-1}	33.6	3.2	3.9	3.9
Diethyl ether	20	1.8×10^{-2}	5.3×10^{-2}	17.0	15.7	9.7	10.7
Diisopropyl ether	20	1.9×10^{-3}	3.3×10^{-2}	17.3	21.9	12.8	17.9
Ethyl acetate	20	1.6×10^{-2}	1.4×10^{-1}	23.9	10.1	7.1	6.8
Heptaldehyde	20	3.4×10^{-3}	—	26.6	—	10.1	13.7
Heptylic acid	20	3.8×10^{-4}	2.7×10^{-1}	28.0	6.1	7.9	7.7
Hexane	25	2.9×10^{-5}	6.0×10^{-4}	19.1	50.1	50.3	50.0
Methyl <i>n</i> -butyl ketone	20	5.0×10^{-3}	1.8×10^{-1}	25.0	9.1	8.9	9.7
Methyl ethyl ketone	25	5.6×10^{-2}	3.5×10^{-1}	24.8	3.1	2.2	3.0
<i>n</i> -Octane	20	3.0×10^{-6}	9.0×10^{-4}	21.8	47.2	50.5	50.8
<i>n</i> -Octanol	20	8.9×10^{-5}	2.5×10^{-1}	27.5	6.7	8.3	8.5
Toluene	20	1.0×10^{-4}	2.5×10^{-3}	27.6	39.6	34.9	36.1
Trichloroethane	20	2.1×10^{-3}	1.9×10^{-3}	34.1	37.0	37.6	37.4
				Avg. error = 15.4%		11.8%	
				Max. error = 48.5%		38.6%	

Sources: Experimental values from Refs. 3, 6, and 7.

(3) From Eq. 21-1:

$$\begin{aligned}\sigma_{ow} &= -3.33 - 7.21 (-0.89) \\ &= 3.1 \text{ dynes/cm}\end{aligned}$$

Within the limits of graphical accuracy, the same value is obtained from Figure 21-1. The experimental value is 3.0; hence, the error is +3.3%.

Example 21-2 Estimate the interfacial tension of benzene and water, assuming that experimental mutual solubility data are not available.

(1) From Chapter 11, the calculated infinite dilution activity coefficient, γ^∞ , for benzene in water is 2094; for water in benzene, $\gamma^\infty = 329$. From Chapter 3 (Eq. 3-11), the solubility of benzene in water is given by $X_o = 1/\gamma^\infty = 1/2094 = 4.8 \times 10^{-4}$. From Figure 3-3 of Chapter 3, the solubility of water in benzene is estimated as $X_w = 3.3 \times 10^{-3}$.

$$(2) \quad X_o + X_w = 4.8 \times 10^{-4} + 3.3 \times 10^{-3} = 3.8 \times 10^{-3}$$

$$\ln(X_o + X_w) = -5.6$$

(3) From Eq. 21-1:

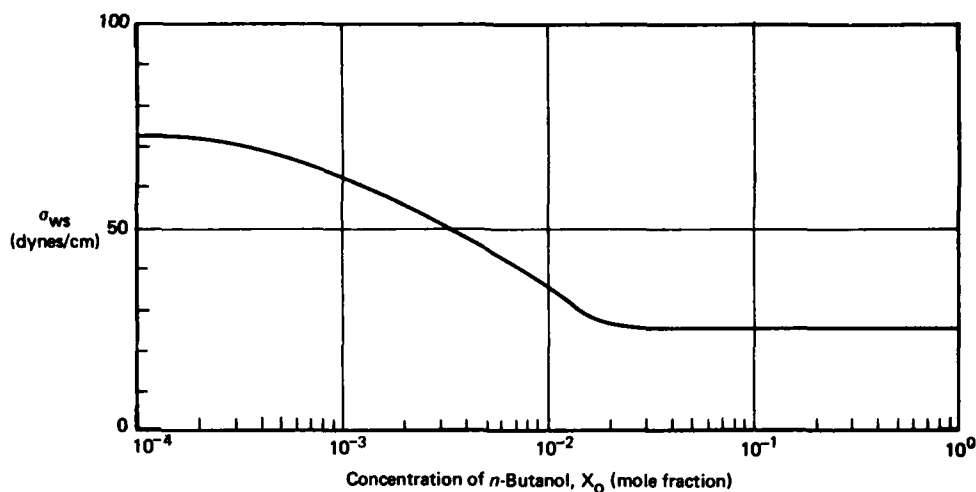
$$\begin{aligned}\sigma_{ow} &= -10/3 - 7.21 (-5.6) \\ &= 37 \text{ dynes/cm}\end{aligned}$$

A similar value is obtained from Figure 21-1. The experimental value is 33.9 dynes/cm, indicating an error of +8.8%. (The use of measured values of X_o and X_w would have yielded an estimated σ_w of 34.6 dynes/cm, as shown in Table 21-2.)

21-4 METHOD 2

The second method utilizes Eq. 21-2. Proper interpretation of Antonov's rule requires that only saturated phase surface tensions be used. This requirement can be relaxed somewhat with respect to the organic phase saturated with water. Figure 21-2 is a typical plot of saturated phase or mixture surface tension as a function of concentration for the system *n*-butanol-water. Notice that an X_o of only 0.01 mole fraction reduces the surface tension of the solution by a factor of ≈ 2 . However, for $X_o > 0.03$ ($X_w < 0.97$), the mixture surface tension is nearly as low as that of pure *n*-butanol. Thus, the substitution of σ_o for σ_w in Eq. 21-2 should result in relatively minor errors.

Methods of estimating mixture surface tensions have been reviewed in Ref. 9. The most versatile method was first proposed by Tamura et



Source: Meissner, H.P. and A.S. Michaels, "Surface Tensions of Pure Liquids and Liquid Mixtures," *Ind. Eng. Chem.*, 41, 2782-87 (1949).

FIGURE 21-2 Mixture Surface Tension of *n*-Butanol – Water

al. [10]. The basic equation is the Macleod-Sugden correlation¹ as applied to mixtures. For a binary mixture and neglecting vapor densities,

$$\sigma_m^{1/4} = \frac{\rho_{Lm}}{M_m} (P_o X_o^w + P_w X_w^w) \quad (21-4)$$

where

σ_m	=	surface tension of mixture
ρ_{Lm}	=	density of mixture
M_m	=	molecular weight of mixture
P_o, P_w	=	parachors for organic component and water
X_o^w, X_w^w	=	mole fractions of organic component and water

The significant concentrations and densities were taken to be those characteristic of the surface layer. Thus, the mixture density is replaced by a hypothetical liquid molar volume $(V^\sigma)^{-1}$. V^σ is estimated from

$$V^\sigma = X_o^\sigma V_o + X_w^\sigma V_w \quad (21-5)$$

where

X_o^σ, X_w^σ	=	mole fractions of the organic component and water in the surface layer
--------------------------	---	--

1. The Macleod-Sugden correlation is discussed in some detail in Chapter 20.

V_o, V_w = pure component molar volumes

Using the definition of the parachor, Tamura *et al.* rewrote Eq. 21-4 as

$$\sigma_m^{1/4} = \psi_w^\sigma \sigma_w^{1/4} + \psi_o^\sigma \sigma_o^{1/4} \quad (21-6)$$

where $\psi_w^\sigma = X_w^\sigma V_w / V^\sigma$ is the hypothetical volume fraction of water in the surface layer. Similarly, for the organic phase, $\psi_o^\sigma = X_o^\sigma V_o / V^\sigma$. By assuming an equilibrium between the surface and bulk phases, the authors were able to estimate ψ_w^σ and ψ_o^σ . The final equation is

$$\log \frac{(\psi_w^\sigma)^p}{\psi_o^\sigma} = \log \frac{(\psi_w)^\sigma}{\psi_o} + \frac{0.441 q}{T} \left(\frac{\sigma_o V_o^{2/3}}{q} - \sigma_w V_w^{2/3} \right) \quad (21-7)$$

where:

ψ_w = bulk volume fraction of water = $X_w^\sigma V_w / (X_o^\sigma V_o + X_w^\sigma V_w)$

ψ_o = bulk volume fraction of organic material = $X_o^\sigma V_o / (X_o^\sigma V_o + X_w^\sigma V_w)$

σ_o, σ_w = pure component surface tensions of organic phase and water

T = temperature (K)

p, q = constants, characteristic of the organic compound

and

$$\psi_o^\sigma + \psi_w^\sigma = 1 \quad (21-8)$$

$$X_o^\sigma + X_w^\sigma = 1 \quad (21-9)$$

When Eq. 21-7 is solved for ψ_w^σ and ψ_o^σ and these values are substituted in Eq. 21-6, the resulting estimates of σ_m (the mixture surface tension) are quite good for hydrocarbons but very poor for polar and hydrogen-bonded materials. For the compounds listed in Table 21-2, interfacial tensions estimated from these values of σ_m deviate from measured values by an average of only 2% for the first group but 260% for the second. This problem is related to the value assigned to p , which was identical to q in Tamura's original paper. We have found, however, that if p is arbitrarily set equal to 1.0, good estimates of σ_m are obtained for all classes of materials, and the subsequent estimates of interfacial tension have average errors of 11.8%.

Table 21-3 lists values of q for various compound classes. Once σ_m for the organic component in water is determined, it can be substituted directly for σ_{os} in Eq. 21-2. Also, as shown earlier, σ_{ws} is very nearly equal to σ_o . Table 21-2, which compares calculated and experimental values of σ_{ow} , shows that method 2 is substantially more accurate than method 1.

TABLE 21-3
Values of q for Equation 21-7

Compound Class	$q^{a,b}$
Acids, alcohols, esters, primary amines	$4N/5$
Hydrocarbons (aliphatic and aromatic), ethers	$2N/3$
Ketones and aldehydes	$1.833 + N/3$
Perhalogenated aliphatic hydrocarbons	N
Monohalogenated aromatics	$2N/3$

a. N = number of carbon atoms.

b. The values of q listed were determined by the author of this chapter and differ from those given by Tamura *et al.* [10]. However, these values appear to fit the experimental data and also extend the method to more classes of materials.

Basic Steps

- (1) Draw structure of organic component. This will assist in the determination of q in Step 5.
- (2) Obtain the solubility of the organic component in water (X_o^w) in mole fraction. If solubility data are not available, they may be estimated using methods outlined in Chapters 2, 3, and 11.
- (3) Obtain the pure component surface tension of the organic phase (σ_o). (If a measured value is not available, see estimation methods in Chapter 20.) Also obtain the surface tension of water (σ_w), which is listed as a function of temperature in numerous handbooks. An abbreviated list is presented in Table 21-4.

TABLE 21-4

Surface Tension of Water at Various Temperatures

Temperature (°C)	σ_w (dynes/cm)
5	74.9
10	74.2
15	73.5
20	72.8
25	72.0
30	71.2
40	69.6

Source: Weast[11]

- (4) Obtain values of the molar volume (V_o and V_w) in cm^3 . This can be easily computed from available density data.² Again, data for water are available for a range of temperatures. Over the temperature range of 5-40°C, however, the density of water varies by only 0.008 g/cm^3 (1.00 g/cm^3 to 0.992 g/cm^3). If density or volume data for the organic component are not available, they may be estimated using the methods of Chapter 19.
- (5) Obtain q from Table 21-3.
- (6) Substitute these values in Eq. 21-7. From the definition of ψ_w and ψ_o , $\psi_w/\psi_o = X_w^w V_w/X_o^w V_o$. Note that $X_w^w = 1 - X_o^w$.
- (7) Calculate ψ_o^g from Eq. 21-7, with $p = 1$. Note that $\psi_o^g = 1 - \psi_w^g$.
- (8) Calculate σ_m from Eq. 21-6 and set equal to σ_{os} in Eq. 21-2. Assume that $\sigma_{ws} = \sigma_o$.
- (9) Calculate σ_{ow} using Eq. 21-2.

Example 21-3 Estimate the interfacial tension between methyl ethyl ketone (MEK) and water at 25°C. The molecular weights are 72.10 and 18.02, respectively.

- (1) The structure of MEK is $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_2\text{H}_5$; hence $N = 4$.
- (2) The solubility of MEK in water (X_o^w) is 5.6×10^{-2} mole fraction [7].

2. $V (\text{cm}^3) = \text{molecular weight (g)}/\text{density (g/cm}^3\text{)}$.

- (3) At 25°C, the surface tension of MEK (σ_o) is 24.8 dynes/cm [7], and the surface tension of water (σ_w) is 72.0 dynes/cm.
- (4) At 25°C, the density of water (ρ_w) is 0.997 g/cm³; hence, its molar volume (V_w) is 18.1 cm³. Similarly, for MEK, $\rho_o = 0.81$ g/cm³ [11] and $V_o = 89.0$ cm³.
- (5) From Table 21-3, $q = 1.833 + (4/3) = 3.17$

$$(6) \quad \frac{\psi_w}{\psi_o} = \frac{X_w^w V_w}{X_o^w V_o} = \frac{0.944 \times 18.1}{0.056 \times 89.0} = 3.43$$

Substituting in Eq. 21-7,

$$\begin{aligned} \log \frac{\psi_w^\sigma}{\psi_o^\sigma} &= \log (3.43) + \frac{0.441 \times 3.17}{298} \left[\frac{24.8 (89.0)^{2/3}}{3.17} - 72 (18.1)^{2/3} \right] \\ &= 0.535 - 1.595 \\ &= -1.06 \end{aligned}$$

$$(7) \quad \frac{\psi_w^\sigma}{\psi_o^\sigma} = \frac{\psi_w^\sigma}{1 - \psi_w^\sigma} = \text{antilog} (-1.06) = 0.087$$

Solving for ψ_w^σ ,

$$\psi_w^\sigma = 0.080$$

$$\psi_o^\sigma = 1 - \psi_w^\sigma = 0.920$$

- (8) From Eq. 21-6,

$$\begin{aligned} \sigma_m^{1/4} &= 0.080 (72.0)^{1/4} + 0.920 (24.8)^{1/4} \\ &= 2.28 \end{aligned}$$

$$\sigma_m = (2.28)^4 = 27.0 = \sigma_{os}$$


$$\sigma_{ws} = \sigma_o = 24.8$$

- (9) From Eq. 21-2,

$$\sigma_{ow} = |27.0 - 24.8| = 2.2$$

The experimental value is 3.0; hence, the error is -27%.

Example 21-4 Estimate the interfacial tension between benzene and water at 25°C using estimated values of the input parameters for the organic component.

- (1) The structure of benzene is: 
- (2) The solubility of benzene in water (X_o^w) was estimated in Example 21-2 as 4.8×10^{-4} mole fraction.
- (3) The estimated surface tension of benzene (σ_o) is 27 dynes/cm (see Chap. 20, method 2). For water, $\sigma_w = 72$ dynes/cm.
- (4) Using method 2 of Chap. 20, the molar volume at the normal boiling point, V_b , is estimated at 98 cm^3 . By the Grain method outlined in Chapter 19, the molar volume of benzene (V_o) at 298K is 90.8 cm^3 . V_w is, as in Example 21-3, 18.1 cm^3 .
- (5) From Table 21-3, $q = 2(6)/3 = 4$.
- (6) $X_w^w = 1 - X_o^w = 0.9995$. Therefore,

$$\frac{\psi_w}{\psi_o} = \frac{0.9995 \times 18.1}{4.8 \times 10^{-4} \times 90.8} = 415$$

Substituting in Eq. 21-7,

$$\begin{aligned} \log \frac{\psi_w^\sigma}{\psi_o^\sigma} &= \log(415) + \frac{0.441(4)}{298} \left[\frac{27(90.8)^{2/3}}{4} - 72(18.1)^{2/3} \right] \\ &= 2.62 - 2.13 \\ &= 0.49 \end{aligned}$$

- (7) $\psi_o^\sigma = 1 - \psi_w^\sigma$. Thus,

$$\frac{\psi_w^\sigma}{1 - \psi_w^\sigma} = \text{antilog}(0.49) = 3.1$$

Solving for ψ_w^σ ,

$$\begin{aligned} \psi_w^\sigma &= 0.76 \\ \psi_o^\sigma &= 1 - 0.76 = 0.24 \end{aligned}$$

- (8) From Eq. 21-6,

$$\begin{aligned} \sigma_m^{1/4} &= 0.76(72)^{1/4} + 0.24(27)^{1/4} \\ &= 2.8 \\ \sigma_m &= (2.8)^4 = 61 = \sigma_{os} \\ \sigma_{ws} &= \sigma_o = 27 \end{aligned}$$

(9) From Eq. 21-2,

$$\sigma_{ow} = |61 - 27| = 34$$

This agrees with the experimental value of 33.9 within the limits of accuracy of the calculation.

21-5 AVAILABLE DATA

Limited data on the interfacial tension between organic liquids and water can be obtained from the references listed in Appendix A. Somewhat more extensive compilations are given in Refs. 3, 6, and 7.

21-6 SYMBOLS USED

- a = constant in Eq. 21-1
- b = constant in Eq. 21-1
- M = molecular weight (g/mol)
- N = number of carbon atoms (Table 21-3)
- P = parachor
- p = parameter in Eq. 21-7
- q = parameter in Eq. 21-7
- T = temperature (K)
- V = molar volume (cm³)
- V_b = molar volume at the normal boiling point (cm³)
- V^σ = hypothetical surface molar volume
- X_o = solubility of organic phase in water (mole fraction)
- X_w = solubility of water in the organic phase (mole fraction)
- X_o^σ = mole fraction of the organic phase in the surface layer
- X_w^σ = mole fraction of water in the surface layer
- X_o^w = mole fraction of organic component in the water phase
- X_w^w = mole fraction of water component in the water phase = 1 - X_o^w

Greek

- φ = parameter in Eq. 21-3
- ψ = bulk volume fraction
- ψ^σ = volume fraction in surface layer

ρ_{Lm}	=	mixture liquid density (g/cm ³)
σ_m	=	surface tension of mixture (dynes/cm)
σ_o	=	pure component surface tension of organic phase (dynes/cm)
σ_{os}	=	surface tension of water saturated with organic phase (dynes/cm)
σ_{ow}	=	interfacial tension (dynes/cm)
σ_w	=	pure component surface tension of water (dynes/cm)
σ_{ws}	=	surface tension of organic phase saturated with water (dynes/cm)

Subscripts

m	=	mixture
o	=	organic phase
w	=	water

Superscripts

σ	=	surface layer
w	=	water phase

21-7 REFERENCES

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22

LIQUID VISCOSITY

Clark F. Grain

22-1 INTRODUCTION

The viscosity of a liquid is a measure of the forces that work against movement or flow when a shearing stress is applied. It has an important bearing on several problems relating to the transfer or movement of bulk quantities of the liquid. For example, a knowledge of the viscosity is required in formulas relating to the pumpability of a liquid, the rate of flow (e.g., from a tank), or spreading (e.g., on water) of a chemical spill. However, as the solutions to these formulas are not very sensitive to variations in viscosity, the focus of this chapter is on estimation methods that yield reasonable accuracy from a minimum of input data. More accurate methods have been developed, but the input data they generally require are available for relatively few chemicals.

Viscosity is commonly reported in units of centipoise (cp)¹ and is represented by the symbol η (subscript L for liquids). Values of η_L for organic liquids generally range from 0.3 to 20 cp at ambient temperatures. Water has a viscosity of 1 cp at 20°C.

Gas viscosity is rather well understood: the viscous force is related to the transfer of momentum as the gas molecules collide and thus is based on the kinetic theory. The theory of liquid viscosity, on the other hand, is

1. 1 cp = 0.01 poise = 0.01 g/s.cm.

not yet firmly established. The molecules in a liquid are held together much more strongly than in a gas. Here, viscosity may be thought of as a measure of the force needed to overcome the mutual attraction of the molecules so that they can be displaced relative to each other. The more strongly the molecules are held together, the smaller the flow for a given shearing stress. With increasing temperature, the random kinetic energy of the molecules helps to overcome the intermolecular forces and reduces the viscosity.

The theories that have developed around this main theme include the following:

- Van der Waals [20] and Andrade [1] assumed that the viscous force is due to transfer of momentum, which is strongly influenced by molecular forces;
- Prandtl [16] and Taylor [18] assumed the viscous force to be molecular in nature but computed it from a mechanical analogy;
- Eyring [5] also considered the force to be molecular in nature but computed it on the basis of chemical kinetics.

Thorough reviews of the various theories have been given by Gemant [9] and Brush [3]. In all of the theories mentioned, the temperature dependence of liquid viscosity, η_L , is described by an equation of the form

$$\eta_L = Ae^{B/T} \quad (22-1)$$

This general form has been verified for a wide variety of liquids and forms the basis for most estimation techniques [17].

In recent years Hildebrand [10] has argued that liquid viscosity is not a direct function of temperature and instead is dependent upon the molar volume. He modified an equation due to Bachinski [2] such that

$$\frac{1}{\eta_L} = \phi = B_2 \left(\frac{V - V_0}{V_0} \right) \quad (22-2)$$

where ϕ is the fluidity, V the molar volume, V_0 the molar volume when $\phi = 0$, and B_2 a constant. Equation 22-2 has been tested with several nonpolar liquids and has been found to be adequate [4,11].

For estimation purposes, however, Eq. 22-2 is somewhat limited in that it applies only to nonpolar liquids and requires measured or estimated data on molar volume as a function of temperature. Furthermore, the constants B_2 and V_0 can be reliably estimated for straight-chain hydrocarbons only.

22-2 AVAILABLE ESTIMATION METHODS

This chapter is limited to a consideration of estimation methods for pure substances below their boiling points. Estimation methods for liquid mixtures are discussed by Reid *et al.* [17]. In considering estimation methods, we have excluded those that require extensive experimental data. Most of these are mere curve-fitting schemes designed to reproduce the viscosity/temperature relationship accurately. Quite often, extrapolation of the analytical expression outside the range of the experimental data base leads to erroneous results. Furthermore, these empirical equations can only be used for a limited number of liquids. Partington [15] and Brush [3] list several of these equations.

Where adjustable parameters are required, we have featured the methods that allow one to estimate the parameters either from structure alone or from some readily available physical property.

Table 22-1 lists the methods considered and brief comments about their limitations. In the following section the recommended methods are analyzed with respect to ease of use and reliability.

22-3 SELECTION OF APPROPRIATE METHOD

A good estimation method should be easy to use, require a minimum amount of input data, and be reasonably accurate. The three methods recommended in this section satisfy these criteria. The first is strictly graphical and requires a knowledge of the viscosity, η_L , at some temperature, T . A means of estimating viscosity at the normal boiling point, T_b , is given.

The other two methods are simply ways of estimating the constants in Eq. 22-1 using either a knowledge of the molecular structure or a knowledge of T_b and the heat of vaporization at that temperature.

Many other methods exist and have been reviewed by Gambill [7] and by Reid, Prausnitz and Sherwood [17]. However, all require a knowledge of the variation of density with temperature and/or the critical constants, T_c and V_c .

TABLE 22-1
Methods for Estimating Liquid Viscosity

Method	Formula ^b	Input ^b	Range	Remarks
Method 1 Lewis and Squires [12] ^a	Graphical	Viscosity at one temp.	0-2 cp	Approximate only; limited range
Method 2 van Velzen <i>et al.</i> [21] ^a	$\log \eta_L = B_3 \left(\frac{1}{T} - \frac{1}{T_o} \right)$	Structure	0-15 cp	S compounds cannot be treated; B ₃ and T _o estimated from structure
Method 3 Grain ^a	$\ln \left(\frac{\eta_L}{\eta_{Lb}} \right) = \frac{(\Delta H_{vb} - RT)}{n} \left(\frac{1}{T} - \frac{1}{T_b} \right)$	T _b	0-15 cp	η_{Lb} , ΔH_{vb} , and n estimated from structure
Orrick and Erbar [14]	$\ln \left(\frac{\eta_L}{\rho_L^M} \right) = A_1 + B_1/T$	ρ_L , A ₁ , B ₁	0-15 cp	N, S compounds cannot be treated; A ₁ and B ₁ estimated by group contributions
Thomas [19]	$\log \left(8.569 \frac{\eta_L}{\rho_L^{1/2}} \right) = \theta \left(\frac{1}{T} - 1 \right)$	ρ_L , θ , T _c	0-15 cp	N, S compounds cannot be treated; θ estimated by group contributions
Hildebrand [10]	$\frac{1}{\eta_L} = B_2 \left(\frac{V - V_o}{V_o} \right)$	V, V _o , B ₂		Limited to nonpolar compounds, V _o and B ₂ estimated from structure
Morris [13]	$\log \left(\frac{\eta_L}{\eta_+} \right) = J \left(\frac{1}{T} - 1 \right)$	T _c , η_+ , J	0-15 cp	η_+ and J estimated from group contributions; S compounds cannot be treated

a. Methods recommended in this chapter.

b. See § 22-7 for definition of symbols.

The recommended methods are described in the three sections that follow. The first and the third are the most general and can be applied to almost any organic liquid. While both require information on the normal boiling point and the viscosity at that temperature, these properties can be estimated if they are not known.

Method 2 requires no experimental data, only a knowledge of the molecular structure; thus, it would appear to be the most attractive of the three. However, it is not applicable to sulfur or phosphorus compounds and nitriles. Also, as noted by van Velzen *et al.* [21], the method is unsatisfactory for the first members of a homologous series.

In Table 22-2 the viscosity estimated by each of the methods is compared with experimental values for a representative list of liquids. It is apparent that method 1 is appropriate only for viscosities up to about 2 cp, a rather limited range. Estimates made outside this range are generally much too high; however, for viscosities within the range, the method offers a rapid and simple means of estimation. This table also shows the average and maximum deviations, in percent, for each of the recommended methods. Values obtained outside the range of validity of the method were excluded.

22-4 METHOD 1

Derivation. The method described here was first proposed by Lewis and Squires [12] and has been found to be reasonably accurate as long as one datum point is known. It is based on the exponential relationship between viscosity and temperature set forth in Eq. 22-1. This equation implies that a curve of the kind shown in Figure 22-1 can be used to estimate the viscosity of any chemical at any temperature, given its viscosity at some other temperature. Thus, for example, if the viscosity at 0°C is 0.7 cp, its value at 100°C is 0.2 cp. The problem, however, is obtaining the single datum; a convenient point is the viscosity at the normal boiling point, η_{Lb} . Approximate values of η_{Lb} for a wide variety of liquids (estimated by the author) are listed in Table 22-3. If the normal boiling point is not known, one of the estimation techniques described in Chapter 12 of this handbook may be used.

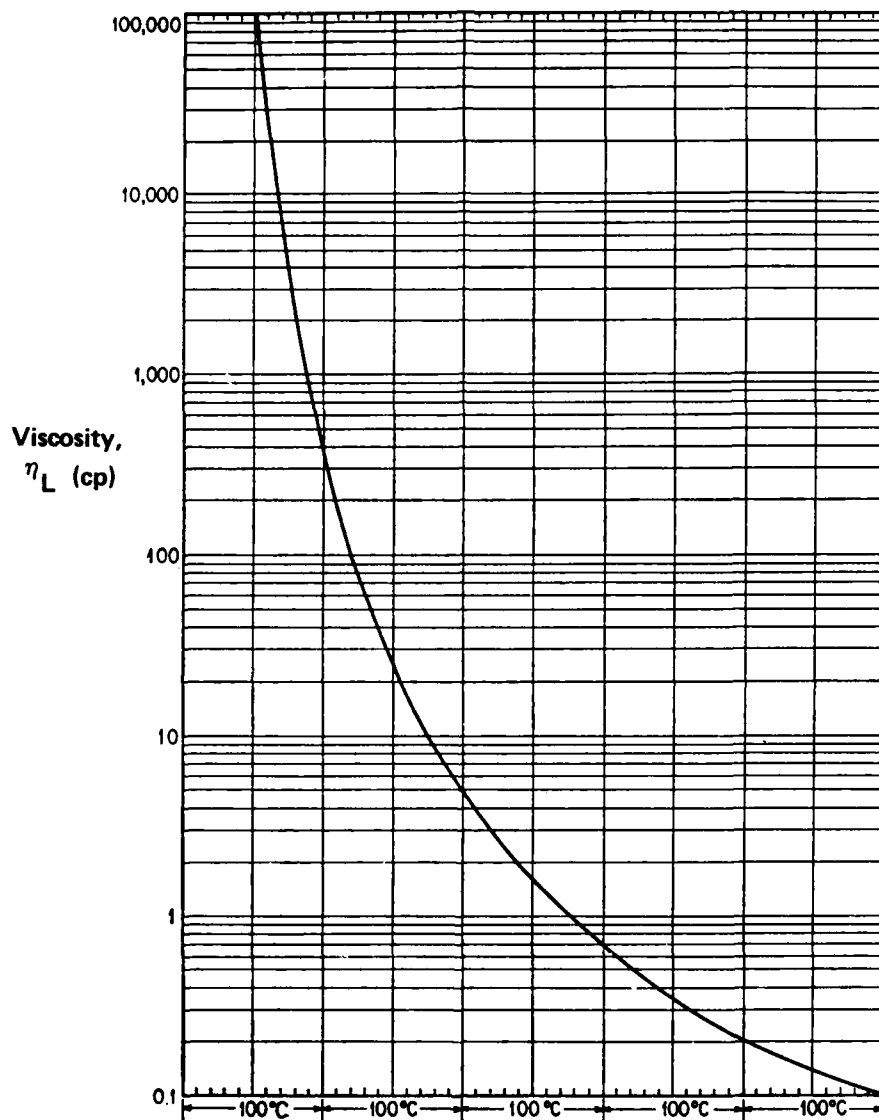
TABLE 22-2

Comparison of Calculated and Experimental Liquid Viscosities

Compound	Temperature (°C)	Viscosity, η_L (cp)			
		Exp. ^a	Method 1	Method 2	Method 3
Hexane	-60	0.89	1.1	0.93	0.85
Hexadecane	20	3.34	40.0	2.95	2.02
Ethanol	0	1.77	1.8	2.26	1.68
n-Butanol	40	1.77	1.8	1.77	1.65
Ethylene glycol	20	19.9	25.0	4.1	12.9
Diethylamine	25	0.35	0.3	0.35	0.31
Acetone	-90	2.10	1.7	1.67	2.64
	0	0.39	0.4	0.38	0.39
Valeric acid	20	2.30	2.2	2.20	2.30
Stearic acid	70	11.6	300.0	12.3	10.9
Chloroform	20	0.56	0.4	0.60	0.65
Butyl acetate	0	1.00	1.1	0.95	1.36
Acetonitrile	25	0.35	0.4	—	0.43
Carbon disulfide	20	0.36	0.3	—	0.26
Benzene	5	0.83	0.64	0.64	0.56
Toluene	20	0.59	0.6	0.41	0.64
Phenol	50	3.0	5.0	2.3	3.1
Aniline	- 5	13.4	30.0	6.4	11.8
	20	4.4	9.0	3.4	5.9
Benzophenone	55	4.67	20.0	5.1	2.7
Bromobenzene	15	1.20	1.5	1.04	1.46
Nitrobenzene	20	2.03	4.0	1.52	2.63
Average Error (%)			19 ^b	22	19
Maximum Error (%)			49 ^b	79	49

a. From Ref. 17, 21 and 22.

b. Calculated values for aniline, benzophenone, hexadecane and stearic acid were not included in these computations. Values of η_L for these compounds are outside of the applicable range for Method 1. If ethylene glycol is also excluded, the average error is still ~ 19%.



Source: Gambill [8]

FIGURE 22-1 Variation of Viscosity with Temperature

TABLE 22-3

Values of η_{Lb} to be Used with Figure 22-1

Substance	η_{Lb} (cp)
Alcohols (aliphatic and aromatic) ^a	0.45
Primary amines (aliphatic and aromatic)	0.45
All other organic liquids ^b	0.2

a. Not applicable to triols.

b. Exceptions are benzene ($\eta_{Lb} = 0.3$) and cyclohexane ($\eta_{Lb} = 0.4$).**Basic Steps**

- (1) Estimate η_{Lb} using Table 22-3 if a measured value is not available.
- (2) Determine temperature difference $\Delta t = t_b - t$, where t_b is the boiling point in $^{\circ}\text{C}$.
- (3) Locate η_{Lb} in Figure 22-1.
- (4) Move Δt degrees to the left along the abscissa and locate the corresponding value of η_L .

Example 22-1 Estimate the viscosity of n-butanol at 0°C and 40°C .

- (1) Table 22-3 lists $\eta_{Lb} = 0.45$ at the boiling point of n-butanol (117.71°C).
- (2) Locate the point corresponding to a viscosity of 0.45 cp on the curve in Figure 22-1.
- (3) For 0°C , $\Delta t = 118 - 0 = 118^{\circ}\text{C}$. Find the point on the curve that is 118° to the left of the point determined in (2) above. The new point corresponds to a viscosity of $\eta_L = 4$ cp. (The measured value of this viscosity is 5.1 cp, indicating a deviation of -22% for the estimated value.)
- (4) Similarly, at 40°C , $\Delta t = 78^{\circ}\text{C}$ and $\eta_L = 1.8$ cp. (Since the measured viscosity listed in Table 22-2 is 1.77 cp, the deviation of this estimated value is only 1.7%.)

Example 22-2 Estimate the viscosity of n-hexane at -60°C and at 0°C .

- (1) From Table 22-3, $\eta_{Lb} = 0.2$ cp.
- (2) Locate the point corresponding to a viscosity of 0.2 cp on the curve in Figure 22-1.
- (3) Since the normal boiling point of n-hexane is 69°C , $\Delta t = 129^{\circ}$ for $t = -60^{\circ}\text{C}$.
- (4) Find the point on the curve that is 129° to the left of the point determined in (2) above. The new point corresponds to a viscosity of $\eta_L = 1.1$ cp. (This is a deviation of +18% from the measured value of 0.89 cp listed in Table 22-2.)
- (5) For 0°C , $\Delta t = 69^{\circ}$. The corresponding viscosity from Figure 22-1 is 0.45 cp. (Since the measured viscosity is 0.38 cp, the deviation is again +18%.)

22-5 METHOD 2

Derivation. The estimation method described here was introduced by van Velzen *et al.* [21]. It is based on the use of Eq. 22-1 at a temperature (T_0) at which $\eta_L = 1$, so that the equation can be rewritten as $1 = Ae^{B/T_0}$, or

$$\log \eta_L = 0 = A_3 + (B_3/T_0) \quad \left| \eta_L = 1 \right. \quad (22-3)$$

whence

$$A_3 = -B_3/T_0$$

At any other temperature T ,

$$\log \eta_L = B_3 \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (22-4)$$

Note that T and T_0 are absolute temperatures.

For straight-chain hydrocarbons containing N carbon atoms, the authors found that the values of B_3 and T_0 could be described by the following equations:

$$N \leq 20 \quad \begin{cases} B_3 = 24.79 + 66.885 N - 1.3173 N^2 - 0.00377 N^3 & (22-5) \\ T_0 = 28.86 + 37.439 N - 1.3547 N^2 + .02076 N^3 & (22-6) \end{cases}$$

$$N > 20 \quad \begin{cases} B_3 = 530.59 + 13.740 N & (22-7) \\ T_0 = 8.164 N + 238.59 & (22-8) \end{cases}$$

For molecules other than straight-chain hydrocarbons, N is replaced by the "equivalent chain length," NE ; this is the chain length of a hypothetical n -alkane with viscosity equal to 1 cp at the temperature at which the viscosity of the compound in question is also 1 cp. NE is calculated as the sum of N (the total number of carbon atoms) and one or more structural and/or configurational factors:

$$NE = N + \sum_i \Delta N_i \quad (22-9)$$

Similarly, B_s is calculated as

$$B_s = B_a + \Delta B \quad (22-10)$$

where B_a is the value of B for the hypothetical alkane with equivalent chain length NE and ΔB is a correction factor that varies with the structure of the compound.

If the compound contains two or more functional groups, the ΔN correction must be multiplied by the number of groups. The ΔB correction is applied only once, regardless of the number of functional groups.

Once NE is known, B_a can be calculated from Eq. 22-5 or 22-7 and T_o is found via either Eq. 22-6 or 22-8. Table 22-4 lists the functions for ΔN and ΔB for various functional groups and structural configurations.

Basic Steps

- (1) Count the number of carbon atoms (N) in the molecular formula.
- (2) Determine the ΔN correction using Table 22-4.
- (3) Sum N and ΔN to obtain NE .
- (4) Calculate B_a by substituting NE in Eq. 22-5 or 22-7 as appropriate.
- (5) Determine the ΔB correction from Table 22-4 and add this to B_a to obtain B_s .
- (6) Calculate T_o by substituting the value of NE in Eq. 22-6 or 22-8 as appropriate.
- (7) Use the calculated values of T_o and B_s in Eq. 22-4 to obtain $\log \eta_L$ at temperature T . Taking the antilog yields η_L .

TABLE 22-4

Functions for ΔN and ΔB

FUNCTIONAL GROUPS	ΔN	ΔB
<i>n</i> -Alkanes		
Alkene	$-0.152 - 0.042N$	$-44.94 + 5.410NE$
Acid $3 \leq N \leq 10$	$6.795 + 0.365N$	$-249.12 + 22.449NE$
$N > 10$	10.71	$-249.12 + 22.449NE$
Ester	$4.337 - 0.230N$	$-149.13 + 18.695NE$
Primary alcohol	$10.606 - 0.276N$	$-589.44 + 70.519NE$
Secondary alcohol	$11.200 - 0.605N$	497.58
Tertiary alcohol	$11.200 - 0.605N$	928.83
Diol	Alcohol correction	557.77
	+ configurational factor	
Ketone	$3.265 - 0.122N$	$-117.21 + 15.781NE$
Ether	$0.298 + 0.209N$	$-9.39 + 2.848NE$
Primary amine	$3.581 + 0.325N$	$25.39 + 8.744NE$
Secondary amine	$1.390 + 0.461N$	$25.39 + 8.744NE$
Tertiary amine ^a	3.27	$25.39 + 8.744NE$
Fluoride	1.43	5.75
Chloride	3.21	-17.03
Bromide	4.39	$-101.97 + 5.954NE$
Iodide	5.76	-85.32
Aromatic and 1-nitro	$7.812 - 0.236N$	$-213.14 + 18.330NE$
2-Nitro	5.84	$-213.14 + 18.330NE$
3-Nitro	5.56	$-338.01 + 25.086NE$
4,5-Nitro	5.36	$-338.01 + 25.086NE$

CONFIGURATIONAL FACTORS

Correction for Aromatic Nucleus

Alkyl-, halogen-, nitrobenzenes, secondary and tertiary amines $8 \leq N \leq 15$	0.60	$-140.04 + 13.869NE$
$N > 15$	$3.055 - 0.161N$	$-140.04 + 13.869NE$
Acids	4.81	$-188.40 + 9.558NE$
Esters	$-1.174 + 0.376N$	$-140.04 + 13.869NE$
Alcohols: OH attached to nucleus: take for all phenolic compounds $NE = 16.17^b$		213.68
Alcohols: OH in side chain	-0.16	213.68
Ketones	2.70	$-760.65 + 50.478NE$
Ethers: take for all aromatic ethers $NE = 11.50^b$		$-140.04 + 13.869NE$
Primary amines: NH_2 attached to nucleus: take for all anilinic compounds $NE = 15.04^b$		

(Continued)

TABLE 22-4 (Continued)

	ΔN	ΔB
Correction for Aromatic Nucleus (Cont'd.)		
Primary amines: NH_2 in side chain	- 0.16	
Polyphenyls	- $5.340 + 0.815N$	-188.40 + 9.558NE
Ortho configuration: OH group present	0.51	-571.94
Without OH		54.84
Meta configuration	0.11	27.25
Para configuration	- 0.04	- 17.57
Cyclopentane $7 \leq N \leq 15$	$0.205 + 0.069N$	- 45.96 + 2.224NE
$N > 15$	$3.971 - 0.172N$	-339.67 + 23.135NE
Cyclohexane $8 \leq N \leq 16$	1.48	-272.85 + 25.041NE
$N > 16$	$6.517 - 0.311N$	-272.85 + 25.041NE
Iso Configuration		
Alkanes	$1.389 - 0.238N$	15.51
Double iso in alkanes (extra correction)	0.93	
Alkenes	$1.389 - 0.238N$	8.93
Alcohols	0.24	94.23
Esters, alkylbenzenes, halogenides, ketones	- 0.24	8.93
Acids	- 0.24	
Ethers, amines	- 0.50	8.93
Various		
$\text{C}(\text{Cl})_x$ configuration	$1.91 - 1.459X$	- 26.38
-CCl-CCl-	0.96	
-C(Br) $_x$	0.50	81.34 - 86.850X
-CBr-CBr-	1.60	- 57.73
CF_3 - (in alcohols)	- 3.93	341.68
(other compounds)	- 3.93	25.55
Diols	- $2.50 + N$	See alcohols

a. Includes pyridine.

b. Other substituents, such as Cl, CH_3 , and NO_2 , are neglected for the determination of NE. For the calculation of B_3 , they have to be taken into account.

Source: van Velzen *et al.* [21].

Example 22-3 Find the viscosity of valeric acid at 20°C (293K).

- (1) The molecular formula of valeric acid, C_4H_9COOH , indicates that $N = 5$.
- (2) Table 22-4 lists the ΔN correction for acids with less than 10 carbon atoms as $6.795 + 0.365N$. For $N = 5$, $\Delta N = 8.62$.
- (3) $NE = N + \Delta N = 13.62$.
- (4) From Eq. 22-5,

$$B_a = 24.79 + 66.885(13.62) - 1.3173(13.62)^2 - 0.00377(13.62)^3$$

$$= 681.86$$
- (5) From Table 22-4, $\Delta B = -249.12 + 22.449NE$

$$= 56.64$$
- (6) $B_3 = B_a + \Delta B = 681.86 + 56.64 = 738.50$
- (7) From Eq. 22-6,

$$T_o = 28.86 + 37.439(13.62) - 1.3547(13.62)^2 + 0.02076(13.62)^3$$

$$= 339.93K$$
- (8) Substituting the above values of B_3 , T , and T_o in Eq. 22-4,

$$\log \eta_L = 738.50(1/293 - 1/339.93)$$

$$= 0.347$$

Therefore, $\eta_L = \text{antilog}(0.347) = 2.22 \text{ cp}$. (The experimentally measured viscosity of valeric acid at 20°C is listed in Table 22-2 as 2.30 cp. The value estimated above thus has a deviation of -3.5%.)

Example 22-4 Find the viscosity of chloroform at 20°C.

- (1) Since the chloroform molecule contains 1 carbon atom, $N = 1$.
- (2) Table 22-4 lists two ΔN corrections for $CHCl_3$:
 - Each chloride functional group requires a correction of 3.21
 - The $C(Cl)_x$ configuration requires a correction of $1.91 - 1.495(x) = -2.47$
- (3) $NE = N + \Delta N = 1 + 3(3.21) - 2.47 = 8.16$
- (4) From Eq. 22-5, $B_a = 480.81$
- (5) Two ΔB corrections are also given in Table 22-4:
 - The chloride functional groups require a correction of -17.03
 - The $C(Cl)_x$ configuration requires a correction of -26.38
- (6) $B_3 = B_a + \Delta B = 480.81 + (-17.03 - 26.38) = 437.40$

(7) From Eq. 22-6, $T_o = 255.44\text{K}$

(8) Using Eq. 22-4,

$$\log \eta_L = 437.40(1/293 - 1/255.44) \\ = -0.2195$$

$$\eta_L = \text{antilog}(-0.2195) \\ = 0.603 \text{ cp}$$

Since Table 22-2 lists an experimental value of 0.56 cp, the estimated value has a deviation of +7.1%.

Example 22-5 Find the viscosity of benzophenone at 55°C.

(1) For $(\text{C}_6\text{H}_5)_2\text{CO}$, $N = 13$.

(2) The ΔN corrections (Table 22-4) are:

- $3.265 - 0.122(13)$ for the ketone functional group
- $2.70(2)$ for the two aromatic nuclei

$$(3) \quad NE = 13 + 3.265 - 1.586 + 5.40 \\ = 20.08$$

$$(4) \quad \text{From Eq. 22-7, } B_a = 530.59 + 13.740(20.08) \\ = 806.49$$

(5) The ΔP corrections (Table 22-4) are:

- $-117.21 + 15.781(20.08)$ for the ketone functional group
- $-760.65 + 50.478(20.08)$

$$(6) \quad B_3 = B_a + \Delta B = 806.49 - 117.21 + 316.88 - 760.65 + 1013.60 \\ = 1259.11$$

(7) From Eq. 22-8, $T_o = 402.5\text{K}$

(8) Using Eq. 22-4,

$$\log \eta_L = 1259.11(1/328 - 1/402.5) \\ = 0.7105$$

$$\eta_L = \text{antilog}(0.7105) \\ = 5.13 \text{ cp}$$

(Table 22-2 lists an experimental value of 4.67 cp; thus, the estimated viscosity has a deviation of +10.0%.)

22-6 METHOD 3

Derivation. The third method can be considered a variation of method 2 or even an analytical extension of method 1. The method is simply based on applying Eq. 22-3 at the normal boiling point, T_b . Thus,

$$\ln \eta_{Lb} = A_4 + (B_4/T_b) \quad (22-11)$$

and

$$A_4 = \ln \eta_{Lb} - (B_4/T_b) \quad (22-12)$$

Hence, at any other temperature T ,

$$\ln \eta_L = \ln \eta_{Lb} + B_4 \left(\frac{1}{T} - \frac{1}{T_b} \right) \quad (22-13)$$

The viscosity at T_b is found from Table 22-3. Following the ideas of Eyring [5], we equate the parameter B_4 to the energy of vaporization such that

$$B_4 = \Delta E_v/n \quad (22-14)$$

where n is an integer. For an ideal gas, the energy of vaporization is related to the heat of vaporization as follows:

$$\Delta E_v = \Delta H_v - RT \quad (22-15)$$

Thus

$$B_4 = \frac{1}{n} (\Delta H_v - RT) \quad (22-16)$$

As a first approximation, the heat of vaporization at the normal boiling point, ΔH_{vb} , can be substituted for ΔH_v . We can then use the method developed by Fishtine [6], in which ΔH_{vb} is given by

$$\Delta H_{vb} = K_F \cdot T_b (8.75 + R \ln T_b) \quad (22-17)$$

where R is the gas constant (1.987 cal/mol-degree) and K_F is a constant. From a consideration of the dipole moments of several compounds, Fishtine derived a table (presented earlier as Table 14-4) that relates the value of K_F to structure.

Combining Eqs. 22-17 and 22-16, we obtain

$$B_4 = \frac{1}{n} [K_F T_b (8.75 + R \ln T_b) - RT] \quad (22-18)$$

Appropriate values of n are given in Table 22-5.

TABLE 22-5

Values of n (Equation 22-18)

Compound Type	n
Aliphatic hydrocarbons	8
Ketones (aliphatic and aromatic)	7
All other organic compounds	5

Basic Steps

- (1) Obtain η_{Lb} from Table 22-3.
- (2) Obtain K_F from Table 14-4.
- (3) Obtain n from Table 22-5.
- (4) Obtain the normal boiling point from either the CRC handbook [22] or from Ref. 17. If T_b is unavailable, it may be estimated by one of the techniques given in Chapter 12.
- (5) Calculate B_4 by using Eq. 22-18.
- (6) Calculate $\ln \eta_L$ at temperature T (K) using Eq. 22-13. The antilog yields η_L .

Example 22-6 Find the viscosity of hexane at -60°C (213K).

- (1) From Table 22-3, $\eta_{Lb} = 0.2$ cp
- (2) From Table 14-4, $K_F = 1.0$
- (3) From Table 22-5, $n = 8$
- (4) From the CRC Handbook [22], $T_b = 342\text{K}$
- (5) Substituting the above values in Eq. 22-18,

$$B_4 = \frac{1}{8} [1.0 \times 342 (8.75 + 1.987 \ln (342)) - (1.987 \times 213)]$$

$$= 817$$

(6) From Eq. 22-13,

$$\ln \eta_L = \ln (0.2) + 817 \left(\frac{1}{213} - \frac{1}{342} \right)$$

$$= -0.16$$

$$\eta_L = 0.85 \text{ cp}$$

The experimental value is 0.89 cp. Hence, the deviation is -4.4%.

Example 22-7 Find the viscosity of aniline at -5°C (268K).

(1) $\eta_{Lb} = 0.45 \text{ cp}$ (Table 22-3)

(2) $K_F = 1.16$ (Table 14-4)

(3) $n = 5$ (Table 22-5)

(4) $T_b = 457.4\text{K}$ [22]

(5) Then, using Eq. 22-18,

$$B_4 = \frac{1}{5} [1.16 \times 457.4 (8.75 + 1.987 \ln (457.4)) - (1.987 \times 268)]$$
$$= 2114$$

(6) From Eq. 22-13,

$$\ln \eta_L = \ln (0.45) + 2114 \left(\frac{1}{268} - \frac{1}{457.4} \right)$$

$$= 2.47$$

$$\eta_L = 11.8 \text{ cp}$$

The experimental value is 13.4 cp. Hence, the deviation is -11.9%.

22-7 AVAILABLE DATA

The following sources were used in obtaining experimental liquid viscosity data:

Weast, R.C. (ed.), *CRC Handbook of Chemistry and Physics*, 59th ed., CRC Press, Inc., West Palm Beach, Fla., 1978-1979.

Reid, Prausnitz and Sherwood [17].

Additional sources of experimental data are listed in Appendix A.

22-8 SYMBOLS USED

A_1	=	constant in Table 22-1
A_3	=	constant in Eq. 22-3
A_4	=	constant in Eq. 22-11
B_a	=	constant in Eq. 22-10
B_1	=	constant in Table 22-1
B_2	=	constant in Eq. 22-2
B_3	=	constant in Eq. 22-4
B_4	=	constant in Eq. 22-11
ΔB	=	correction factor in Eq. 22-10
ΔE_v	=	energy of vaporization in Eq. 22-14 (cal/mol)
ΔH_v	=	heat of vaporization in Eq. 22-15 (cal/mol)
ΔH_{vb}	=	heat of vaporization at the normal boiling point in Eq. 22-17 (cal/mol)
J	=	viscosity constant in Table 22-1
K_F	=	constant in Eq. 22-17
M	=	molecular weight (g)
N	=	number of carbon atoms
n	=	integer in Eq. 22-14
ΔN	=	correction factor in Eq. 22-9
NE	=	equivalent chain length in Eq. 22-9
R	=	gas constant (cal/mol·K)
t	=	temperature (°C)
T	=	temperature (K)
T_b	=	temperature at the normal boiling point (K)
T_c	=	critical temperature (K)
T_o	=	temperature at which $\eta_L = 1$ in Eq. 22-3 (K)
T_r	=	ratio in Table 22-1 equal to T/T_c
V	=	molar volume in Eq. 22-2 (cm ³ /mol)
V_c	=	critical volume (cm ³ /mol)
V_o	=	molar volume when $\phi = 0$ in Eq. 22-2 (cm ³ /mol)

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RESEARCH AND DEVELOPMENT OF METHODS FOR ESTIMATING PHYSICOCHEM--ETC(U)

JUN 81 W J LYMAN, W F REEHL, D H ROSENBLATT

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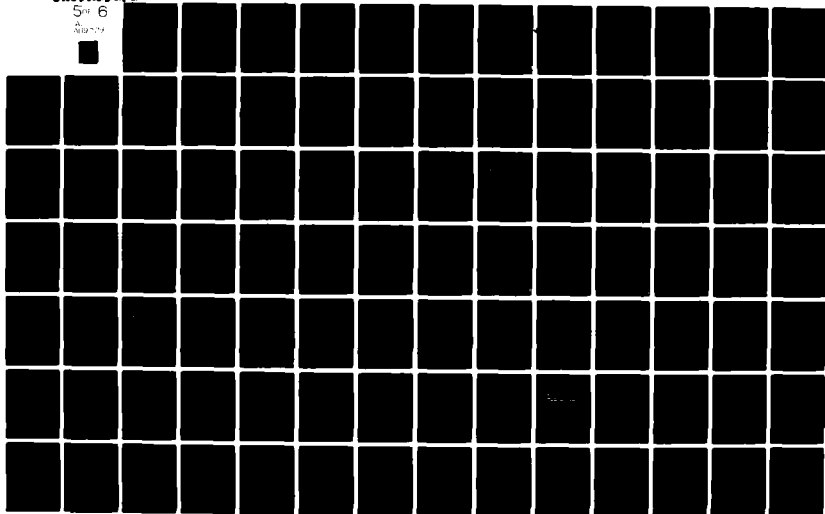
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Greek

- η_+ = pseudo critical viscosity in Table 22-1 (cp)
 η_L = liquid viscosity (cp)
 η_{Lb} = liquid viscosity at the normal boiling point (cp)
 ϕ = fluidity = $1/\eta_L$ in Eq. 22-2 (cp^{-1})
 ρ_L = liquid density in Table 22-1 (g/cm^3)
 θ = constant in Table 22-1

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23

HEAT CAPACITY

James D. Birkett

23-1 INTRODUCTION

Heat capacity, C , is defined as the ratio of the heat absorbed by a system to the resulting temperature increase. It is commonly expressed in calories per gram per degree Celsius ($\text{cal/g}\cdot^\circ\text{C}$) or calories per mole per degree Celsius ($\text{cal/mol}\cdot^\circ\text{C}$).¹ Because C is also a function of temperature, it is the limiting value of the ratio as ΔT approaches zero, and is specified at a given temperature. For gases, two heat capacities may be defined: one, C_{pg} , where heat is absorbed with the system held at constant pressure, and the other, C_{vg} , where heat is absorbed with the system held at constant volume. Thermodynamically, it can be shown [5] that, for ideal gases, the difference in molar heat capacities ($C_{pg} - C_{vg}$) is equal to the gas constant, R ($1.987 \text{ cal/mol}\cdot^\circ\text{C}$). Heat capacities typically range from 25 to 55 $\text{cal/mol}\cdot^\circ\text{C}$ for organic liquids and 15 to 50 $\text{cal/mol}\cdot^\circ\text{C}$ for organic gases at constant pressure.

It can further be shown [5] that $C_{vg} = 3/2R$ and $C_{pg} = 5/2R$ for a monatomic gas whose energy is solely translational. These relationships are borne out experimentally with helium, argon, neon, mercury, and sodium. For polyatomic molecules, however, rotational and vibrational components of energy must also be considered; predictions based only on theory require accurate measurement of spectroscopic parame-

1. Many publications use the notation $\text{cal/g}\cdot\text{mol}\cdot^\circ\text{C}$, which is equivalent to $\text{cal/mol}\cdot^\circ\text{C}$, the notation used in this chapter. Note also that $\text{cal/mol}\cdot^\circ\text{C}$ and $\text{cal/mol}\cdot\text{K}$ are equivalent.

ters (moments of inertia, vibrational frequencies) and lengthy calculations more suited to computerization.

Heat capacities are required for calculating many thermochemical and engineering parameters. The values are obtained either by direct reference to experimental data, which are not always available, or by various empirical estimation methods. Not surprisingly, most of the methods are based on structural considerations, such as the contribution of the component bonds and/or functional groups to the total heat capacity of the molecule. Values contributed by these groups are derived from experimentally determined heat capacities of numerous compounds.

This chapter presents methods for estimating the heat capacity at constant pressure for gases (C_{pg}) and liquids (C_{pl}), as these are most often required when dealing with an organic chemical that has been introduced into the environment. Of particular concern are spills of bulk quantities of organic chemicals. A number of mathematical models have been derived to predict the fate of chemicals after such spills. Heat capacity is a required parameter in models predicting venting rates and the heating and/or cooling of bulk quantities of the chemical under various conditions, e.g., contact with water and exposure to thermal radiation from a fire.

The estimation methods described in this chapter are summarized in Table 23-1. All are group-contribution methods in which the sum of individual group contributions directly yields a value of C . *Thus, the only input information required is the chemical structure.*

All of the recommended methods allow the estimation of heat capacities at ambient temperatures ($\sim 25\text{-}30^\circ\text{C}$). Values of C usually increase with temperature, but for purposes of hazard assessment (chemical spill modeling), changes in C may be considered negligible over the normal range of ambient temperatures.

23-2 ESTIMATION METHODS FOR GASES

There are several methods for estimating C_{pg} , including those of Dobratz and Meghreblian [4,8] and Thinh *et al.* [12]. This chapter recommends two methods — one derived by Rihani and Doraiswamy [11] and the other by Benson [1,2] — which provide good compromises among ease of use, accuracy, and applicability to a wide range of compounds. The first method is based on adding the contribution to C_{pg} of each of the component groups within the molecule; Rihani and Doraiswamy have tabulated values of these contributions for 41 common groups. These

TABLE 23-1

Recommended Methods for Estimating Heat Capacity

Method	Basis	Comments
Gases		
Rihani and Doraiswamy [11]	Group contributions	Errors typically 2-10% Can handle most aromatics, ring systems, conjugated double bonds, triple bonds
Benson, Cruickshank, <i>et al.</i> [2]	Group contributions	Errors typically < 5% Numerous group contributions evaluated; more complex to use than that of Rihani and Doraiswamy
Liquids		
Johnson and Huang [6]	Group contributions	Errors usually < 10% Limited number of group contributions available
Chueh and Swanson [3]	Group contributions	Errors usually < 3% More group contributions available than for Johnson and Huang

contributions are given as the coefficients of a polynomial in temperature, T:

$$C_{pg} = a + bT + cT^2 + dT^3 \quad (23-1)$$

This method is easy to use, if the contributions for all groups present are listed; it generally predicts C_{pg} to within 5% and is often within 2% of measured values. Rihani and Doraiswamy state [11], based on their own calculations including a test set of 36 compounds, that at 300K the average method error is about 3%, while in the temperature range of 400 to 1500K it is less than 2%. In addition, the error for hydrocarbons (1.5%) is less than that for nonhydrocarbons (4%). The procedure is described in §23-3.

Benson's method, applicable only at 300 K, assigns a value to each divalent or polyvalent atom based on the groups or other atoms to which it is bonded. Values have been compiled for most of the groups likely to be encountered. While the method is a bit cumbersome for large and complex molecules, patience is generally rewarded by estimation within 1% of the observed values.

Table 23-2 gives a sampling of C_{pg} values calculated by both of the above methods and compares the results with measured values. The more complex method of Benson, Cruickshank, *et al.* is generally more accurate, but in many cases the added accuracy may not warrant the extra effort involved.

TABLE 23-2
Measured vs. Estimated Heat Capacities for Gases at 300K
(cal/mol·K)

Compound	Literature Value [13]	Estimated C_{pg}			
		Rihani and Doraiswamy [11]	% Error	Benson, Cruickshank, <i>et al.</i> [2]	% Error
2,2-Dimethylpropane	29.21	29.29	+ 0.27	29.13	-0.27
2-Methylbut-1-ene	26.41	27.33	+ 3.5	27.08	+2.5
3-Methyl-1,2-butadiene	25.5	25.38	+ 0.32	24.95	- 1.38
cis 1,3-Pentadiene	22.7	21.57	- 5.0	22.51	-0.84
1,2,3,5-Tetramethylbenzene	44.57	46.94	+ 5.3	44.16	-0.92
o-Methylstyrene	34.9	32.91	- 5.7	35.17	+0.77
Biphenyl	39.05	38.69	- 0.92	39.06	+0.03
p-Cresol	29.8	30.31	+ 1.7	30.02	+0.74
Trimethylene oxide	14.3	15.49	+ 8.3	14.28	-0.14
Methyl ethyl ketone	24.7	24.39	- 1.3	23.47	-5.0
Nitromethane	15.36	13.76	-10.4	15.29	-0.45
1,2-Diodopropane	24.1	25.10	+ 4.1	24.59	+2.0
1,1-Difluoro-2-iodoethene	19.3	17.49	- 9.4	18.5	-4.1
Avg. Error			4.3%		1.5%

23-3 METHOD OF RIHANI AND DORAISWAMY

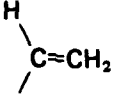
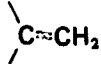
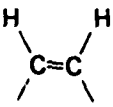
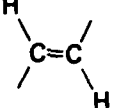
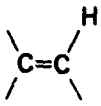
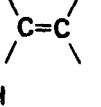
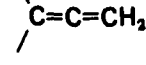
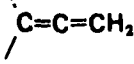
Principles of Use. The method of Rihani and Doraiswamy [11] is the quickest way to estimate C_{pg} for organic gases and is applicable to several broad classes of compounds, including many aromatics, acyclic ring systems, conjugated double bonds, and acetylenes. Table 23-3 lists the bond contributions calculated by Rihani and Doraiswamy.

Basic Steps

- (1) Draw the structure of the compound.
- (2) Find the individual group contributions to the coefficients of Eq. 23-1 in Table 23-3 and add them in proportion to the

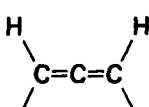


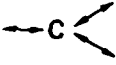



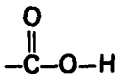
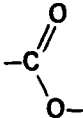

TABLE 23-3

Group Contributions for Eq. 23-1

Group	a	b × 10 ²	c × 10 ⁴	d × 10 ⁶
Aliphatic Hydrocarbon Groups				
—CH ₃	0.6087	2.1433	— 0.0852	0.001135
—CH ₂	0.3945	2.1363	— 0.1197	0.002596
=CH ₂	0.5266	1.8357	— 0.0954	0.001950
—C—H	— 3.5232	3.4158	— 0.2816	0.008015
—C—	— 5.8307	4.4541	— 0.4208	0.012630
	0.2773	3.4580	— 0.1918	0.004130
	— 0.4173	3.8857	— 0.2783	0.007364
	— 3.1210	3.8060	— 0.2359	0.005504
	0.9377	2.9904	— 0.1749	0.003918
	— 1.4714	3.3842	— 0.2371	0.006063
	0.4736	3.5183	— 0.3150	0.009205
	2.2400	4.2896	— 0.2566	0.005908
	2.6308	4.1658	— 0.2845	0.007277





(continued)

TABLE 23-3 (Continued)

Group	a	b × 10 ²	c × 10 ⁴	d × 10 ⁶
Aliphatic Hydrocarbon Groups (cont'd.)				
	- 3.1249	6.6843	- 0.5766	0.017430
≡CH	2.8443	1.0172	- 0.0690	0.001866
-C≡	- 4.2315	7.8689	- 0.2973	0.00993
Aromatic Hydrocarbon Groups				
HC 	- 1.4572	1.9147	- 0.1233	0.002985
-C 	- 1.3883	1.5159	- 0.1069	0.002659
 -C 	0.1219	1.2170	- 0.0855	0.002122
Oxygen-Containing Groups				
-OH	6.5128	- 0.1347	0.0414	- 0.001623
-O-	2.8461	- 0.0100	0.0454	- 0.002728
	3.5184	0.9437	0.0614	- 0.006978
	1.0016	2.0763	- 0.1636	0.004494
	1.4055	3.4632	- 0.2557	0.006886
	2.7350	1.0751	0.0667	- 0.009230
O 	- 3.7344	1.3727	- 0.1265	0.003789
Nitrogen-Containing Groups				
-C≡N	4.5104	0.5461	0.0269	- 0.003790
-N≡C	5.0860	0.3492	0.0259	- 0.002436
-NH ₂	4.1783	0.7378	0.0679	- 0.007310

(continued)

TABLE 23-3 (Continued)

Group	a	b × 10 ²	c × 10 ⁴	d × 10 ⁶
Nitrogen-Containing Groups (cont'd.)				
	- 1.2530	2.1932	- 0.1604	0.004237
	- 3.4677	2.9433	- 0.2673	0.007828
	2.4458	0.3436	0.0171	- 0.002719
-NO ₂	1.0898	2.6401	- 0.1871	0.004750
Sulfur-Containing Groups				
-SH	2.5597	1.3347	- 0.1189	0.003820
-S-	4.2256	0.1127	- 0.0026	- 0.000072
	4.0824	- 0.0301	0.0731	- 0.006081
-SO ₃ H	6.9218	2.4735	0.1776	- 0.022445
Halogen-Containing Groups				
-F	1.4382	0.3452	- 0.0106	- 0.000034
-Cl	3.0660	0.2122	- 0.0128	0.000276
-Br	2.7605	0.4731	- 0.0455	0.001420
-I	3.2651	0.4901	- 0.0539	0.001782
Contributions Due to Ring Formation				
3-membered ring	- 3.5320	- 0.0300	0.0747	- 0.005514
4-membered ring	- 8.6550	1.0780	0.0425	- 0.000250
5-membered ring				
Pentane	- 12.2850	1.8609	- 0.1037	0.002145
Pentene	- 6.8813	0.7818	- 0.0345	0.000591
6-membered ring				
Hexane	- 13.3923	2.1392	- 0.0429	- 0.001865
Hexene	- 8.0238	2.2239	- 0.1915	0.005473

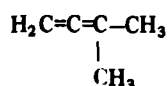
Source: Rihani and Doraiswamy [11].

number of such groups in the molecule. Include ring contributions if necessary.

- (3) Substitute the coefficients in Eq. 23-1 and calculate C_{pg} using the appropriate value of T (K).
- (4) The total is in units of cal/mol·K (25°C). To convert to units of cal/g·K (same as cal/g·°C), divide by the molecular weight.

Example 23-1 Calculate C_{pg} for 3-methyl-1,2-butadiene at 300K. (Although this compound is a liquid at room temperature, C_{pg} for the vapors over the liquid can still be calculated.)

- (1) The molecular structure is:



- (2) The group contributions from Table 23-3 are:

	a	$b \times 10^2$	$c \times 10^4$	$d \times 10^6$
$2[-\text{CH}_3]:$	$2(0.6087)$	$2(2.1433)$	$2(-0.0852)$	$2(0.001135)$
$[>\text{C}=\text{CH}_2]:$	<u>2.6308</u>	<u>4.1658</u>	<u>-0.2845</u>	<u>0.007277</u>
	3.8482	8.4524	-0.4549	0.009547

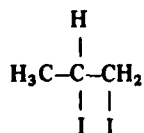
- (3) Substituting in Eq. 23-1, with $T = 300\text{K}$:

$$\begin{aligned} C_{pg} &= 3.8482 + 8.4524 \times 10^{-2} (300) - 0.4549 \times 10^{-4} (300)^2 \\ &\quad + 0.009547 \times 10^{-6} (300)^3 \\ &= 25.38 \text{ cal/mol}\cdot^\circ\text{C} \end{aligned}$$

The literature value of C_{pg}^{300} is 25.3 cal/mol·°C [13], and thus the calculated value is within 0.3%.

Example 23-2 Calculate C_{pg} for 1,2-diiodopropane at 300K.

- (1) The molecular structure is:



(2) The bond contributions from Table 23-3 are:

	a	b × 10 ²	c × 10 ⁴	d × 10 ⁶
[—CH ₃]:	0.6087	2.1433	−0.0852	0.001135
$\begin{array}{c} \\ \text{[—CH]:} \\ \end{array}$	−3.5232	3.4158	−0.2816	0.008015
$\begin{array}{c} \\ \text{[—CH}_2\text{]:} \\ \end{array}$	0.3945	2.1363	−0.1197	0.002596
2[—I]:	$\frac{2(3.2651)}{4.0102}$	$\frac{2(0.4901)}{8.6756}$	$\frac{2(−0.0539)}{−0.5943}$	$\frac{2(0.001782)}{0.1531}$

(3) Substituting in Eq. 23-1:

$$\begin{aligned}
 C_{pg} &= 4.0102 + 8.6756 \times 10^{-2} (300) - 0.5943 \times 10^{-4} (300)^2 \\
 &\quad + 0.01531 \times 10^{-6} (300)^3 \\
 &= 25.10 \text{ cal/mol} \cdot ^\circ\text{C}
 \end{aligned}$$

The literature value of C_{pg}^{300} is 24.1 cal/mol·°C [13], indicating an error of 4.1%.

23-4 METHOD OF BENSON, CRUICKSHANK, et al.

Principles of Use. The method of Benson, Cruickshank, *et al.* [2] is considerably more complex than the preceding method, but its greater accuracy and utility become apparent with a little practice. Instead of focusing on each group within the molecule, as specified by the atoms connected therein, it deals with each atom, as differentiated by the number and type of bonds to neighboring atoms. The contributions of each such atom are then combined to give the total C_{pg} . Corrections are also made for the presence of certain overall structures, such as rings.

Table 23-4 lists the contributions at 300K (27°C) and various correction terms. Use of the table requires not only knowledge of the molecular structure but also familiarity with the notational system employed. (See footnotes to the table.) For molecules with both *trans* and *cis* isomers, contributions are tabulated for the *trans* form, which is generally the more stable. However, a *cis* correction is given, as well as one for *ortho* positioning of functional groups on aromatic compounds. Corrections are also given for some ring compounds, due to the strain imposed by such configurations on "normal" bond angles.

TABLE 23-4
Benson Group Contributions to Heat Capacities at 300K

A. Basic Hydrocarbon Groups^{a,b}

Group	Contribution	Group	Contribution	Group	Contribution
C—(C)(H) ₃	6.19	C _d —(C _t)(C)	4.40	C—(C _B)(C) ₃	(4.37)
C—(C) ₂ (H) ₂	5.50	C—(C _d)(H) ₃	6.19	C—(C _B) ₂ (C)(H)	3.74
C—(C) ₃ (H)	4.54	C—(C _d) ₂ (H) ₂	(4.7)	C—(C _B) ₂ (C) ₂	3.57
C—(C) ₄	4.37	C—(C _d) ₂ (C) ₂	3.57	C—(C _B)(C _d)(H) ₂	(4.7)
		C—(C _d)(C) ₃	(3.99)	C _t —(H)	5.27
C _d —(H) ₂	5.10	C—(C _d)(C)(H) ₂	5.12	C _t —(C)	3.13
C _d —(C)(H)	4.16	C—(C _d)(C) ₂ (H)	(4.16)	C _t —(C _d)	(2.57)
C _d —(C) ₂	4.10	C—(C _d) ₂ (C)(H)	3.74	C _t —(C _B)	2.57
C _d —(C _d)(H)	4.46	C—(C _t)(H) ₃	6.19		
C _d —(C _d)(C)	(4.40)	C—(C _t)(C)(H) ₂	4.95	C _B —(H)	3.24
C _d —(C _B)(H)	4.46	C—(C _t)(C) ₂ (H)	(3.99)	C _B —(C)	2.67
C _d —(C _B)(C)	(4.40)			C _B —(C _d)	3.59
C _d —(C _t)(H)	4.46	C—(C _B)(H) ₃	6.19	C _B —(C _t)	3.59
		C—(C _B)(C)(H) ₂	5.84	C _B —(C _B)	3.33
		C—(C _B)(C) ₂ (H)	(4.88)		
				C _a	3.9

Correction for Next-Nearest Neighbor

Cis	-1.34
Ortho	1.12

Corrections for Ring Compounds

Cyclopropane	-3.05
Cyclobutane	-4.61
Cyclobutene	-2.53
Cyclopentane	-6.5
Cyclopentene	-5.98
Cyclopentadiene	-4.3
Cyclohexane	-5.8
Cyclohexene	-4.28

B. Oxygen-containing Compounds^{a,b}

Group	Contribution	Group	Contribution	Group	Contribution
CO—(CO)(H)	6.72	CO—(C _B)(C)	5.68	O—(CO)(C _d)	1.44
CO—(CO)(C)	5.46	CO—(C _B)(H)	6.40	O—(CO)(C)	3.90
CO—(O)(C _d)	5.97	CO—(C) ₂	5.59	O—(CO)(H)	3.81
CO—(O)(C _B)	2.18	CO—(C)(H)	7.03	O—(O)(C)	(3.7)
CO—(O)(C)	5.97	CO—(H) ₂	8.47	O—(O) ₂	(3.7)
CO—(O)(H)	7.03	O—(C _B)(CO)	2.06	O—(O)(H)	5.17
CO—(C _d)(H)	7.03	O—(CO) ₂	-0.41	O—(C _d) ₂	3.4
CO—(C _B) ₂	5.26	O—(CO)(O)	3.7	O—(C _d)(C)	3.4

(continued)

TABLE 23-4 (Continued)

B. Oxygen-containing Compounds (Continued)

Group	Contribution	Group	Contribution	Group	Contribution
O—(C _B) ₂	1.09	C _d —(O)(H)	4.16	C—(O) ₂ (C)(H)	5.06
O—(C _B)(C)	3.4	C _B —(CO)	2.67	C—(O) ₂ (H) ₂	2.83
O—(C _B)(H)	4.3	C _B —(O)	3.9	C—(O)(C _B)(H) ₂	3.71
O—(C) ₂	3.4	C—(CO) ₂ (H) ₂	5.60	C—(O)(C _B)(C)(H)	5.14
O—(C)(H)	4.33	C—(CO)(C) ₂ (H)	6.21	C—(O)(C _d)(H) ₂	4.66
C _d —(CO)(O)	5.59	C—(CO)(C)(H) ₂	6.2	C—(O)(C) ₃	4.33
C _d —(CO)(C)	3.73	C—(CO)(C) ₃	5.07	C—(O)(C) ₂ (H)	4.80
C _d —(CO)(H)	3.79	C—(CO)(H) ₃	6.19	C—(O)(C)(H) ₂	4.99
C _d —(O)(C _d)	(4.40)	C—(O) ₂ (C) ₂	1.59	C—(O)(H) ₃	6.19
C _d —(O)(C)	4.10				

Strain or Ring Corrections

Ether oxygen, gauche		-0.10
Ditertiary ethers		-3.94
Ethylene oxide		-2.0
Trimethylene oxide		-4.6
Tetrahydrofuran		-4.25
Tetrahydropyran		-4.28
1,3-Dioxane		-2.51
1,4-Dioxane		-4.16
1,3,5-Trioxane		1.79

Furan		-4.19
Dihydropyran		-4.44
Cyclopentanone		-8.53
Cyclohexanone		-8.10
Succinic anhydride		-7.90
Glutaric anhydride		-7.93
Maleic anhydride		-5.12

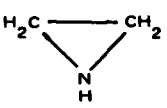
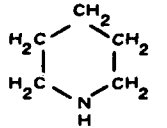
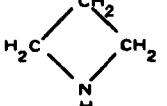
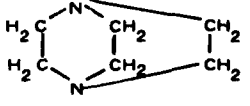
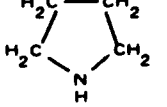
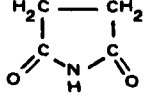
(continued)

TABLE 23-4 (Continued)

C. Nitrogen-containing Compounds^{a,c}

Group	Contribution	Group	Contribution	Group	Contribution
C—(N)(H) ₃	6.19	N—(C _B)(H) ₂	5.72	C—(CN)(C)(H) ₂	11.10
C—(N)(C)(H) ₂	5.25	N—(C _B)(C)(H)	3.82	C—(CN)(C) ₂ (H)	11.00
C—(N)(C) ₂ (H) ²	4.67	N—(C _B)(C) ₂	0.62	C—(CN)(C) ₃	8.65
C—(N)(C) ₃	4.35	N—(C _B) ₂ (H)	2.16	C—(CN) ₂ (C) ₂	14.72
N—(C)(H) ₂	5.72	C _B —(N)	3.95	C _d —(CN)(H)	9.80
N—(C) ₂ (H)	4.20	N _A —(N)	2.12	C _d —(CN)(C)	9.74
N—(C) ₃	3.48	CO—(N)(H)	7.03	C _d —(CN) ₂	13.60
N—(N)(H) ₂	6.10	CO—(N)(C)	5.37	C _d —(NO) ₂ (H)	12.3
N—(N)(C)(H)	4.82	N—(CO)(H) ₂	4.07	C _B —(CN)	9.8
N—(N)(C) ₂	1.56	N—(CO)(C)(H)	3.87	C _t —(CN)	10.30
N—(N)(C _B)(H)	3.28	N—(CO)(C) ₂	1.83	C—(NO ₂)(C)(H) ₂	12.59
N _i —(H)	2.95	N—(CO)(C _B)(H)	3.03	C—(NO ₂)(C) ₂ (H)	11.99
N _i —(C)	2.48	N—(CO) ₂ (H)	3.59	C—(NO ₂)(C) ₃	9.89
N _i —(C _B)	2.60	N—(CO) ₂ (C)	1.07	C—(NO ₂) ₂ (C)(H)	17.32
N _A —(H)	4.38	N—(CO) ₂ (C _B)	0.98	O—(NO)(C)	9.10
N _A —(C)	2.70			O—(NO ₂)(C)	9.54

Ring Corrections

Ethylenimine		-2.07	Piperidine		-0.56
Azetidine		-4.73	C ₆ H ₁₂ N ₂		-9.44
Pyrrolidine		-6.17	Succinimide		2.16

(continued)

TABLE 23-4 (Continued)

D. Halogen Groups^a

Group	Contribution	Group	Contribution	Group	Contribution
C—(F) ₃ (C)	12.7	C—(I)(H)(C) ₂	9.2	C _d —(I)(H)	8.8
C—(F) ₂ (H)(C)	9.9	C—(I)(C)(C _d)(H)	8.13	C _d —(C)(Cl)	8.0
C—(F)(H) ₂ (C)	8.1	C—(I)(C _d)(H) ₂	8.82	C _d —(C)(I)	8.9
C—(F) ₂ (C) ₂	9.9	C—(I)(C) ₃	9.83	C _d —(C _d)(Cl)	8.3
C—(F)(H)(C) ₂	7.30	C—(Cl)(Br)(H)(C)	12.4	C _d —(C _d)(I)	9.2
C—(F)(C) ₃	6.80	N—(F) ₂ (C)	8.25	C _t —(Cl)	7.9
C—(F) ₂ (Cl)(C)	13.7	C—(Cl)(C)(O)(H)	9.85	C _t —(Br)	8.3
C—(Cl) ₃ (C)	16.3	C—(I) ₂ (C)(H)	12.69	C _t —(I)	8.4
C—(Cl) ₂ (H)(C)	12.1	C—(I)(O)(H) ₂	8.22	C _B —(F)	6.3
C—(Cl)(H) ₂ (C)	8.9	C _d —(F) ₂	9.7	C _B —(Cl)	7.4
C—(Cl) ₂ (C) ₂	12.2	C _d —(Cl) ₂	11.4	C _B —(Br)	7.8
C—(Cl)(H)(C) ₂	9.0	C _d —(Br) ₂	12.3	C _B —(I)	8.0
C—(Cl)(C) ₃	9.3	C _d —(F)(Cl)	10.3	C—(C _B)(F) ₃	12.5
C—(Br) ₃ (C)	16.7	C _d —(F)(Br)	10.8	C—(C _B)(Br)(H) ₂	9.29
C—(Br)(H) ₂ (C)	9.1	C _d —(Cl)(Br)	12.1	C—(C _B)(I)(H) ₂	9.78
C—(Br)(H)(C) ₂	8.93	C _d —(F)(H)	6.8	C—(Cl) ₂ (CO)(H)	12.8
C—(Br)(C) ₃	9.3	C _d —(Cl)(H)	7.9	C—(Cl) ₃ (CO)	17.0
C—(I)(H) ₂ (C)	9.2	C _d —(Br)(H)	8.1	CO—(Cl)(C)	8.87

Corrections for Next-nearest Neighbors

Ortho (F)(F)	0
Ortho (Cl)(Cl)	-0.50
Ortho (alkane) (halogen)	0.42
Cis (halogen) (halogen)	-0.19
Cis (halogen) (alkane)	-0.97

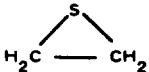
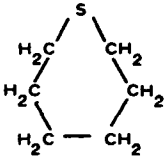
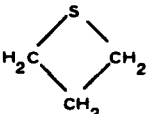
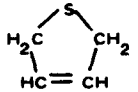
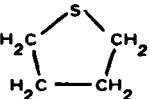
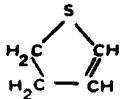
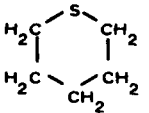
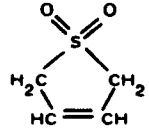
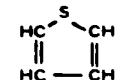
E. Organosulfur Groups^a

Group	Contribution	Group	Contribution	Group	Contribution
C—(H) ₃ (S)	6.19	S—(S) ₂	4.7	SO ₂ —(C _d)(C _B)	9.89
C—(C)(H) ₂ (S)	5.38	C—(SO)(H) ₃	6.19	SO ₂ —(C _d) ₂	11.52
C—(C) ₂ (H)(S)	4.85	C—(C)(SO)(H) ₂	4.55	SO ₂ —(C) ₂	10.18
C—(C) ₃ (S)	4.57	C—(C) ₃ (SO)	3.06	SO ₂ —(C)(C _B)	9.94
C—(C _B)(H) ₂ (S)	4.11	C—(C _d)(SO)(H) ₂	4.40	SO ₂ —(C _B) ₂	8.36
C—(C _d)(H) ₂ (S)	5.00	C _B —(SO)	2.67	SO ₂ —(SO ₂)(C _B)	9.81
C _B —(S)	3.90	SO—(C) ₂	8.88	CO—(S)(C)	5.59
C _d —(H)(S)	4.16	SO—(C _B) ₂	5.72	S—(H)(CO)	7.63
C _d —(C)(S)	3.50	C—(SO ₂)(H) ₃	6.19	C—(S)(F) ₃	9.88
S—(C)(H)	5.86	C—(C)(SO ₂)(H) ₂	5.38	CS—(N) ₂	5.59
S—(C _B)(H)	5.12	C—(C) ₂ (SO ₂)(H)	4.42	N—(CS)(H) ₂	6.07
S—(C) ₂	4.99	C—(C) ₃ (SO ₂)	2.32	S—(S)(N)	3.7
S—(C)(C _d)	4.22	C—(C _d)(SO ₂)(H) ₂	5.00	N—(S)(C) ₂	3.97
S—(C _d) ₂	4.79	C—(C _B)(SO ₂)(H) ₂	3.71	SO—(N) ₂	5.59
S—(C _B)(C)	3.02	C _B —(SO ₂)	2.67	N—(SO)(C) ₂	4.20
S—(C _B) ₂	2.00	C _d —(H)(SO ₂)	3.04	SO ₂ —(N) ₂	5.59
S—(S)(C)	5.23	C _d —(C)(SO ₂)	1.85	N—(SO ₂)(C) ₂	6.02
S—(S)(C _B)	2.89				

(continued)

TABLE 23-4 (Continued)

Ring Corrections

Thiirane		-2.85	Thiacycloheptane		-7.75
Trimethylene sulfide		-4.59	3-Thiocyclopentene		-6.44
Tetrahydrothiophene		-4.90	2-Thiocyclopentene		-6.44
Thiacyclohexane		-6.22	C4H6SO2		-4.90
			Thiophene		-4.90

Notes:

- C_d represents a carbon atom that is joined to another carbon atom by a double bond. It is considered divalent. Example: 2-pentene has the groups $C-(C_d)(H)_3$, $C_d-(C)(H)$ twice, $C-(C_d)(H)_2$, and $C-(C)(H)_3$.

C_t represents a carbon atom that is joined to another carbon atom by a triple bond. It is considered monovalent. Example: propyne has the groups $(C_t)-(H)$, $C_t-(C)$, and $C-(C_t)(H)_3$.

C_B represents a carbon atom in an aromatic ring. It is considered monovalent. Example: p-ethyl toluene has the groups $C-(C)(H)_3$, $C-(C_B)(C)(H)_2$, $C-(C_B)(H)_3$, $C_B-(C)$ twice, and $C_B-(H)$ four times.

C_a represents the allene group, $>C=C=C<$; the end carbons are treated as normal C atoms. Example: 1,2-butadiene has the groups C_a , $C_d-(H)_2$, $C_d-(C)(H)$, and $C-(C_d)(H)_3$.
- Numbers in parentheses are estimated or derived from other than direct experimental data.
- N_1 represents a double-bonded nitrogen in imines. $N_1-(C_B)$ represents a pyridine nitrogen. N_A represents a double-bond nitrogen in azo compounds.

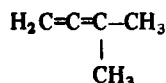
Sources: Benson et al. [2] and Reid et al. [10].

Basic Steps

- (1) Draw the structure of the compound.
- (2) Find the individual group contributions to C_{pg} in Table 23-4 and add them in proportion to the number of such groups in the molecule.
- (3) Add (or subtract, as applicable) any necessary corrections for next-nearest neighbors and ring structures (other than benzene rings).
- (4) The resulting value is in units of $\text{cal/mol} \cdot ^\circ\text{C}$ and applies to a temperature of 300K (27°C). To convert to units of $\text{cal/g} \cdot ^\circ\text{C}$ (same as $\text{cal/g} \cdot \text{K}$), divide by the molecular weight.

Example 23-3 Calculate the C_{pg} of 3-methyl-1,2-butadiene.

- (1) The molecular structure is:



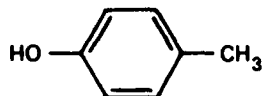
- (2) The group contributions from Table 23-4 are:

$$\begin{array}{ll} \text{C}_d(\text{H})_2 & 5.10 \\ \text{C}_a & 3.90 \\ \text{C}-(\text{C}_d)(\text{C})_2 & 3.57 \\ 2[\text{C}-(\text{C})(\text{H})_3] & 2(6.19) \\ \hline \text{C}_{pg}^{300} & = 24.95 \text{ cal/mol} \cdot ^\circ\text{C} \end{array}$$

The literature value is $25.3 \text{ cal/mol} \cdot ^\circ\text{C}$ [13], indicating an error of -1.4% .

Example 23-4 Calculate the C_{pg} of p-cresol.

- (1) The molecular structure is:



- (2) The group contributions from Table 23-4 are:

$$\begin{array}{ll} 4[\text{C}_B-(\text{H})] & 4(3.24) \\ \text{C}_B-(\text{C}) & 2.67 \end{array}$$

$C_B-(O)$	3.9
$C-(C_B)(H)_3$	6.19
$O-(C_B)(H)$	4.3
<hr/>	
$C_{pg}^{300} = 30.02 \text{ cal/mol}\cdot^\circ\text{C}$	

Since the literature value is $29.8 \text{ cal/mol}\cdot^\circ\text{C}$ [13], the error is 0.74%.

23-5 ESTIMATION METHODS FOR LIQUIDS

Heat capacities of liquids, like those of gases, are estimated from the aggregate contribution of bonds or groups. Included here are the simplified group method of Johnson and Huang [6] and the more complex method of Chueh and Swanson [3].

As noted previously, liquid heat capacity (C_{pl}) usually increases with temperature. However, it is a very weak function of temperature except in the region just below the critical temperature. At ambient temperatures, it can be assumed to be constant for most purposes.

The method of Johnson and Huang generally allows estimation of C_{pl} within 10%, while that of Chueh and Swanson usually involves errors of less than 3%. Table 23-5 compares values of C_{pl} for several organic compounds with those estimated by both methods.

23-6 METHOD OF JOHNSON AND HUANG

Principles of Use. The method of Johnson and Huang [6] is based on molecular structure and requires the identification of various molecular groups and the summation of their contributions to the overall value of C_{pl} . Table 23-6 lists such group contributions at 20°C .

Basic Steps

- (1) Draw the structure of the compound.
- (2) Find the individual group contributions to C_{pl} in Table 23-6 and add them in proportion to the number of such groups in the molecule.
- (3) The value obtained is in units of $\text{cal/mol}\cdot^\circ\text{C}$ at 20°C . To convert to units of $\text{cal/g}\cdot^\circ\text{C}$ (same as $\text{cal/g}\cdot\text{K}$), divide by the molecular weight.

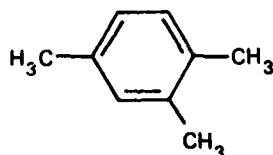
TABLE 23-5

Measured vs. Estimated Heat Capacities for Organic Liquids
(cal/mol·K)

Compound	Literature Value 298K [13]	Estimated C_{p1} at 293K			
		Johnson & Huang [6]	% Error	Chueh & Swanson [3]	% Error
3-Ethylpentane	52.5	54.0	+ 2.8	53.18	+1.3
2,3-Dimethylbutene-2	41.7	38.0	- 8.9	42.8	+2.6
1,2,4-Trimethylbenzene	51.6	53.0	+ 2.7	51.0	- 1.2
Furan	27.4	30.0	+ 9.5	29.6	+8.0
1,1-Dimethylhydrazine	39.2	43.0	+ 9.7	39.1	-0.3
<i>trans</i> -1,2-Dimethylcyclopentane	45.1	49.5	+ 9.8	45.0	-0.2
1,2-Dibromoethane	32.2	20.0	-37.8	32.5	+0.9
Cyclopentylmercaptan	39.5	44.8	+13.4	39.9	+1.0
Ethyl acetate	40.6	40.6	0	39.42	-2.9
sec-Butylmercaptan	40.9	44.7	+ 9.3	40.56	-0.8
Avg. Error			10.4%		1.9%

Example 23-5 Calculate C_{p1} for 1,2,4-trimethylbenzene.

(1) The molecular structure is:



(2) The group contributions from Table 23-6 are:

$$3(\text{CH}_3-) \quad 3(9.9)$$

$$\text{C}_6\text{H}_5- \quad 30.5$$

$$-2(-\text{H}) \quad -2(3.6)$$

$$C_{p1} = 53.0 \text{ cal/mol}\cdot^\circ\text{C}$$

Note that because the ring contribution is for the C_6H_5- group, and the compound has only three hydrogens directly on the ring, the value of two H- groups was *subtracted* from the total. Comparing the result with the measured value of 51.6 at 25°C [13], we find an error of 2.7%. Part of this is attributable to the 5° temperature difference.

TABLE 23-6
Group Heat Capacities for Organic Liquids

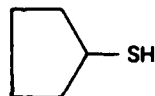
Group	Contribution ^a (cal/mol·°C)
CH ₃ —	9.9
—CH ₂ —	6.3
$\begin{array}{c} \\ -C-H \\ \end{array}$	5.4
—COOH	19.1
—COO—(esters)	14.5
>CO (ketones)	14.7
—CN	13.9
—OH	11.0
—NH ₂ (amines)	15.2
—Cl	8.6
—Br	3.7
—NO ₂	15.3
—O—	8.4
—S—	10.6
C ₆ H ₅ —	30.5
H—(formic acid, formates)	3.55

a. At 20°C only. For certain atomic configurations, it may be necessary to use values for C alone and for H alone; values of 1.76 and 3.6, respectively, appear adequate.

Source: Johnson and Huang [6].

Example 23-6 Calculate C_{p1} for cyclopentylmercaptan.

(1) The molecular structure is:



(2) The group contributions from Table 23-6 are:

4 (—CH ₂ —)	4 (6.3)
—CH—	5.4
—S—	10.6
H—	3.6
	<hr/>
	44.8 cal/mol·°C at 20°C

The literature value is 39.5 [13], indicating an error of about 13%.

23-7 METHOD OF CHUEH AND SWANSON

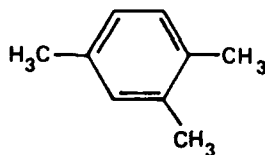
Principles of Use. The method of Chueh and Swanson [3], like that of Johnson and Huang, is based on the principle of aggregating group contributions. While somewhat more complicated, it is generally more accurate: the results are usually within 3% of the experimental values. Contributions at 20°C are shown in Table 23-7. The footnotes and exceptions are important and should be studied carefully. While the method is accurate only at reduced temperatures² below about 0.74, this is rarely a drawback in actual practice.

Basic Steps

- (1) Draw the structure of the compound.
- (2) Find the individual group contributions to C_{p1} in Table 23-7 and add them in proportion to the number of such groups in the molecule.
- (3) The value obtained is in units of cal/mol·°C at 20°C. To convert to units of cal/g·°C (same as cal/g·K), divide by the molecular weight.

Example 23-7 Calculate C_{p1} for 1,2,4-trimethylbenzene.

- (1) The molecular structure is:



- (2) The group contributions from Table 23-7 are:

$$3(\text{ring-CH=}) \quad 3(5.3)$$

$$3(\text{ring-C=}) \quad 3(2.9)$$

$$3(-\text{CH}_3) \quad \underline{3(8.8)}$$

$$C_{p1} = 51.0 \text{ cal/mol}\cdot^\circ\text{C at } 20^\circ\text{C}$$

Since the literature value is 51.6 cal/mol·°C at 25°C [13], the error is only -1.2%.

2. Reduced temperature = (system temperature)/(critical temperature).

TABLE 23-7

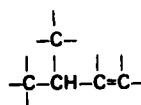
Group Contributions for Molar Liquid Heat Capacity at 20°C

Group	Value	Group	Value	Group	Value
Alkane					
-CH ₃	8.80	-C=O	12.68	-N= (in a ring)	4.5
-CH ₂ -	7.26			-C≡N	13.9
		H		Sulfur	
-CH-	5.00	O		-SH	10.7
				-S-	8.0
-C-	1.76	-C-OH	19.1	Halogen	
		O		-Cl (first or second	8.6
Olefin^a				on a carbon)	
=CH ₂	5.20	-C-O-	14.5	-Cl (third or fourth	6.0
=C-H	5.10	-CH ₂ OH	17.5	on a carbon)	
				-Br	9.0
=C-	3.80	-CHOH	18.2	-F	4.0
Alkyne^a		-COH	26.6	-I	8.6
CH≡	5.90			Hydrogen	
-C≡	5.90	-OH	10.7	H- (for formic acid,	3.5
In a Ring		-ONO ₂	28.5	formates, hydrogen	
		Nitrogen		cyanide, etc.)	
-CH-	4.4	H			
-C= or -C-	2.9	H-N-	14.0		
		H			
-CH=	5.3	-N-	10.5		
-CH ₂ -	6.2				
Oxygen		-N-	7.5		
-O-	8.4				
>C=O	12.66				

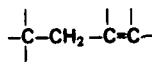
a. Add 4.5 for any carbon group which is joined by a single bond to a second carbon group connected by a double or triple bond to a third carbon group. If a carbon group can meet this criterion in more ways than one, add 4.5 for each time it can do so, with the following exceptions:

- Do not add an extra 4.5 for -CH₃ groups or for a carbon group in a ring.
- For a -CH₂- group fulfilling the 4.5 addition criterion, add 2.5 instead of 4.5. However, when the -CH₂- group fulfills the addition criterion in more ways than one, the addition should be 2.5 the first time and 4.5 for each subsequent addition.

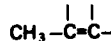
For example:



Add 4.5



Add 2.5

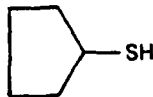


No addition

Source: Chueh and Swanson [3].

Example 23-8 Calculate C_{p1} for cyclopentylmercaptan.

(1) The molecular structure is:



(2) The group contributions from Table 23-7 are:

4(-CH ₂ -)	4(6.2)
-CH-	4.4
-SH	10.7
<hr/>	
$C_{p1} = 39.9 \text{ cal/mol} \cdot ^\circ\text{C at } 20^\circ\text{C}$	

This is within 1% of the literature value of $39.5 \text{ cal/mol} \cdot ^\circ\text{C}$ at 25° [13].

23-8 AVAILABLE DATA

Heat capacity data for both liquids and gases are found in most conventional handbooks; a listing of such handbooks is provided in Appendix A. In addition, the extensive article in *Chemical Reviews* by Benson, Cruickshank *et al.* [2] contains many examples of experimental

23-9 SYMBOLS USED

- a, b, c, d = parameters in Eq. 23-1
C = heat capacity (cal/g·°C or cal/mol·°C)
R = gas constant = 1.987 cal/mol·°C
T = temperature (K)

Subscripts

- pg = gas at constant pressure
vg = gas at constant volume
pl = liquid at constant pressure

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24

THERMAL CONDUCTIVITY

James D. Birkett

24-1 INTRODUCTION

Thermal conductivity, λ , is defined as the quantity of heat which will traverse a medium of unit thickness and cross-sectional area per unit time, under the influence of an applied temperature gradient. In scientific notation, it is expressed as

$$\lambda = \frac{\text{calories} \cdot \text{centimeters of thickness}}{\text{square centimeters of area} \cdot \text{seconds} \cdot \text{K (temperature gradient)}} \quad (24-1)$$

which reduces to

$$\lambda = \text{cal/cm} \cdot \text{s} \cdot \text{K} \quad (24-2)$$

However, the literature abounds in data given in English, engineering, and mixed units; readers will frequently encounter Btu, feet, inches, °F, etc., in various reference works and should be prepared to make the appropriate conversions.

This chapter addresses the estimation of thermal conductivities of organic liquids, λ_L , as this parameter is often required for calculating rates of evaporation of large quantities of spilled liquids. Values of λ_L are usually in the range of $250\text{--}400 \times 10^{-6} \text{ cal/cm} \cdot \text{s} \cdot \text{K}$, but some liquids with a high degree of association, such as may occur with hydrogen bonding, have higher conductivities.

The thermal conductivity of organic liquids is generally estimated by means of equations that utilize other known properties of the material and, to a lesser extent, structural considerations (as with heat capacity in the preceding chapter). Two methods are frequently employed, depending upon the required accuracy (Table 24-1).

TABLE 24-1

Recommended Methods for Estimating Thermal Conductivity

Method	Inputs Required	Method Error ^a	Comments
Sato and Riedel [9] (§ 24-3)	M, T _b , T _c	5.5% [9] 7.0% (Table 24-3)	Convenient to use
Robbins and Kingrea [11] (§ 24-4)	ΔH _{vb} , C _{pℓ} , ρ _ℓ , T _b , T _c , structural parameters	4.8% [9] 12% (Table 24-3)	Not recommended for routine use because of excessive input requirements

a. Average absolute errors for selected test sets. See § 24-2 for details.

Combining the methods of Sato [5] and Riedel [10], Reid *et al.* [9] developed the equation

$$\lambda_{\ell} = \frac{2.64 \times 10^{-3}}{M^{1/2}} \left[\frac{3 + 20(1 - T_r)^{2/3}}{3 + 20(1 - T_{rb})^{2/3}} \right] \quad (24-3)$$

in which only the reduced temperature, T_r (= T/T_c), reduced boiling point, T_{rb} (= T_b/T_c), and molecular weight, M, are needed. While errors may be as much as ± 20%, Eq. 24-3 may be adequate for many purposes and is rapidly calculated.

A more elaborate method has been reported by Robbins and Kingrea [11], who propose the following equation:

$$\lambda_{\ell} = \frac{(88.0 - 4.94H) 10^{-3}}{\Delta S^*} \left(\frac{0.55}{T_r} \right)^N C_{p\ell} \rho_{\ell}^{4/3} \quad (24-4)$$

where

H = structural factor determined from Table 24-2

TABLE 24-2

H Factors for Method of Robbins and Kingrea

Functional Group	Number of Groups	H ^a
Unbranched hydrocarbons:		
Paraffins		0
Olefins		0
Rings		0
F substitutions	1	1
	2	2
Cl substitutions	1	1
	2	2
	3 or 4	3
Br substitutions	1	4
	2	6
I substitutions	1	5
OH substitutions	1 (iso)	1
	1 (normal)	-1
	2	0
	1 (tertiary)	5
CH ₃ branches	1	1
	2	2
	3	3
C ₂ H ₅ branches	1	2
<i>i</i> -C ₃ H ₇ branches	1	2
C ₄ H ₉ branches	1	2
Oxyger. substitutions:		
$\begin{array}{c} \\ -C=O \end{array}$ (ketones, aldehydes)		0
$\begin{array}{c} O \\ \\ -C-O- \end{array}$ (acids, esters)		0
-O- (ethers)		2
NH ₂ substitutions	1	1

a. For compounds containing multiple functional groups, the H-factor contributions are additive.

Source: Robbins and Kingrea [11]

ΔS^*	=	entropy term equal to $\Delta H_{vb}/T_b + R \ln(273/T_b)$
ΔH_{vb}	=	molar heat of vaporization at normal boiling point
ρ_l	=	liquid density
C_{pl}	=	molar liquid heat capacity
R	=	universal gas constant
N	=	$\begin{cases} 1 & \text{for liquids with densities of } < 1 \text{ g/cm}^3 \\ 0 & \text{for liquids of greater density} \end{cases}$

Deviations from experimental values range from a few percent to perhaps 25%. (However, disagreement between separately measured values of λ_l are often this great.)

Several other estimation methods are available; some are discussed by Reid *et al.* [9], and others are described in Refs. 1, 2, 6, 7 and 8.

Thermal conductivity is only weakly a function of temperature, usually decreasing as temperature increases. At ambient conditions, any temperature correction to λ would likely be less than other uncertainties in the calculation.

24-2 METHOD ERRORS

The combined method of Sato and Riedel for the estimation of thermal conductivity requires very little effort and produces results which are generally within a few percent of the literature value. As mentioned earlier, considerable disagreement may be found in the measured literature values, so these may be acceptable deviations. Reid *et al.* [9] provide measured and estimated values using this method for 31 compounds at one or more temperatures. For the 64 data points covered, the errors range from $< 0.1\%$ to 27%, and the average absolute error is 5.5%. An average absolute error of 7.0% was found for the 14 compounds listed in Table 24-3; the errors ranged up to 30%. The method requires only the molecular weight, the boiling point (at normal pressure), and the critical temperature of the compound.

The method developed by Robbins and Kingrea reportedly yields λ_l within 5% of the literature value, with maximum deviations up to 15% [11]. This claim appears justified from the comparison of measured and estimated values (using this method) for 66 data points (32 compounds) given by Reid *et al.* [9].¹ They show errors ranging from $< 0.1\%$ to 28% and an average absolute error of 4.8%. However, for the compounds tested in Table 24-3, this method was not outstandingly accurate

1. The 66 data points included all of those used to test the Sato and Riedel method plus two additional points for ethylene glycol.

TABLE 24-3

Measured vs. Estimated Thermal Conductivities of Organic Liquids
(10^{-6} cal/cm·s·K)

Compound	Literature Value [12]	Estimated λ_l			
		Sato & Riedel	Error (%)	Robbins & Kingrea	Error (%)
Acetaldehyde	393	399	+ 1.5	313	-20
Acetone	385	377	- 2.1	365	- 5.2
Allyl alcohol	430	418	- 2.8		
Aniline	424	369	-13	382	- 9.9
Bromobenzene	266	268	+ 0.8	286	+ 7.5
<i>n</i> -Butyl acetate	327	226	-31		
Carbon tetrachloride	261	251	- 3.8	192	-26
<i>m</i> -Cresol	358	342	- 4.7		
Ethyl ether	328	337	+ 2.7	263	-20
Iodobenzene	242	240	- 0.8	201	-17
<i>N</i> -Methylaniline	442	325	-26		
Toluene	338	345	+ 2.1	324	- 4.1
Triethylamine	289	313	+ 8.3	283	- 2.1
<i>p</i> -Xylene	325	326	+ 0.3		
Average Absolute Error			7.1%		12%

(average error was 12%). The calculation itself is not difficult, but a substantial amount of user time can be spent in obtaining values for the required inputs — the critical and boiling point temperatures, molecular weight, heat of vaporization, liquid heat capacity, molar and gram densities, and a calculated structural value, H . The latter calculation is subject to error, and other properties must often be estimated because of a lack of measured values. For instance, literature values of the liquid heat capacity were readily available for only 9 of the 14 compounds listed in Table 24-3. Among these nine, the error ranged from 2.1% to 26%. In contrast, the conductivities of all 14 could be estimated by the Sato-Riedel method. For this reason, we do not recommend the method of Robbins and Kingrea for routine use.

24-3 METHOD OF SATO AND RIEDEL

The use of this method and the derived equation [9] is very rapid, requiring only the molecular weight, M , and the reduced temperature and boiling point:

$$\lambda_g = \frac{2.64 \times 10^{-3}}{M^{1/2}} \left[\frac{3 + 20(1 - T_r)^{2/3}}{3 + 20(1 - T_{rb})^{2/3}} \right] \quad (24-3)$$

Basic Steps

- (1) Obtain molecular weight, M .
- (2) Look up or estimate critical temperature, T_c , and boiling point, T_b , of the compound. (Methods for estimating T_c and T_b are provided in Chapter 12.)
- (3) Calculate T_r and T_{rb} from the simple relationships $T_r = T/T_c$, $T_{rb} = T_b/T_c$.
- (4) Insert these parameters into Eq. 24-3 and compute λ_g in cal/cm·s·K.

Example 24-1 Calculate λ_g for acetaldehyde at 293K.

- (1) The molecular weight is 44.05.
- (2) $T_c = 461\text{K}$, $T_b = 294\text{K}$ [12]
- (3) $T_r = 293/461 = 0.636$, $T_{rb} = 294/461 = 0.638$

$$(4) \quad \lambda_g = \frac{2.64 \times 10^{-3}}{\sqrt{44.05}} \left[\frac{3 + 20(1 - 0.636)^{2/3}}{3 + 20(1 - 0.638)^{2/3}} \right] = 3.99 \times 10^{-4} \text{ cal/cm} \cdot \text{s} \cdot \text{K}$$

The literature value is 3.93×10^{-4} cal/cm·s·K [12]; thus, the error is 1.5%.

Example 24-2 Calculate λ_g for *m*-cresol at 300K.

- (1) The molecular weight is 108.
- (2) $T_c = 705\text{K}$, $T_b = 475\text{K}$ [12]
- (3) $T_r = 300/705 = 0.426$, $T_{rb} = 475/705 = 0.674$

$$(4) \quad \lambda_g = \frac{2.64 \times 10^{-3}}{\sqrt{108}} \left[\frac{3 + 20(1 - 0.426)^{2/3}}{3 + 20(1 - 0.674)^{2/3}} \right] = 3.42 \times 10^{-4} \text{ cal/cm} \cdot \text{s} \cdot \text{K}$$

The literature value is 3.58×10^{-4} cal/cm·s·K [12]; thus, the error is -4.7%.

24-4 METHOD OF ROBBINS AND KINGREA

This method entails use of the following equation:

$$\lambda_l = \frac{(88.0 - 4.94H) 10^{-3}}{\Delta S^*} \left(\frac{0.55}{T_r} \right)^N C_{pl} \rho_l^{4/3} \quad (24-4)$$

Measured or estimated values must be obtained for C_{pl} , ρ_l , T_c , T_b and ΔH_{vb} . T_r is determined by the relationship $T_r = T/T_c$, and ΔS^* is calculated from the equation

$$\Delta S^* = \Delta H_{vb}/T_b + R \ln (273/T_b) \quad (24-5)$$

H is obtained by adding the contributions from Table 24-2, and N is set at 1 or 0, depending on whether ρ_l is less than or greater than unity, respectively.

Basic Steps

- (1) Obtain the following input parameters:
 Liquid heat capacity, C_{pl} (cal/mol·K)
 Molar liquid density, ρ_l (mol/cm³)
 Critical temperature, T_c (K)
 Boiling point, T_b (K)
 Heat of vaporization at T_b , ΔH_{vb} (cal/mol)
 (Estimation methods for these inputs are available elsewhere in this handbook: C_{pl} , Chapter 23; ρ_l , Chapter 19; T_c , Chapter 12 (§12-4); T_b , Chapter 12; and ΔH_{vb} , Chapter 13.)
- (2) For the temperature of interest, T (K), calculate the reduced temperature, T_r ($= T/T_c$).
- (3) Use Eq. 24-5 to obtain ΔS^* . For the gas constant, R , use 1.987 cal/mol·K.
- (4) Find the appropriate value of H from Table 24-2.
- (5) Set the value of N equal to 1 if $\rho_l < 1.0$ g/cm³ (at 20°C) and equal to 0 if $\rho_l > 1.0$ g/cm³ (at 20°C).
- (6) Substitute all of these input parameters into Eq. 24-4 to obtain λ_l in cal/cm·s·K.

Example 24-3 Calculate λ_l for toluene at 273K.

- (1) From Ref. 12,

$$C_{pl} = 35.6 \text{ cal/mol} \cdot \text{K}, \rho_l = 0.00941 \text{ mol/cm}^3, T_c = 594 \text{ K},$$

$$T_b = 384 \text{ K}, \text{ and } \Delta H_{vb} = 8581 \text{ cal/mol.}$$

- (2) $T_r = 273/594 = 0.460$

(3) From Eq. 24-5,

$$\begin{aligned}\Delta S^* &= 8581/384 + 1.987 \ln (273/384) \\ &= 21.7\end{aligned}$$

(4) Table 24-2 lists a value of l for H, since toluene has one CH_3 branch.

(5) $\rho_l < 1\text{g/cm}^3$. Therefore, $N=1$.

(6) Substituting these values into Eq. 24-4,

$$\begin{aligned}\lambda_l &= \frac{(88.0 - 4.94) 10^{-3}}{21.7} \left(\frac{0.55}{0.46} \right)^1 35.6 (0.00941)^{4/3} \\ &= 0.324 \times 10^{-3} \text{ cal/cm}\cdot\text{s}\cdot\text{K}\end{aligned}$$

Since the literature value [12] of λ_l is $0.338 \times 10^{-3} \text{ cal/cm}\cdot\text{s}\cdot\text{K}$, the error with this method is -4.1% .

24-5 AVAILABLE DATA

Thermal conductivity data are not as readily available as most other physical properties. Conventional handbooks such as Weast [12] list some values, but there are no major literature compilations other than Jamieson [2,3]. Manufacturers' data sheets and similar commercial publications should be consulted when possible. Appendix A lists a few additional sources.

24-6 SYMBOLS USED

C_{pl}	=	molar liquid heat capacity (cal/mol·K)
H	=	structural factor from Table 24-2
ΔH_{vb}	=	molar heat of vaporization at normal boiling point (cal/mol)
M	=	molecular weight (g/mol)
N	=	exponent in Eq. 24-4, (1 for liquid density $< 1\text{g/cm}^3$, 0 for density $> 1\text{g/cm}^3$)
R	=	gas constant (1.987 cal/mol·K)
ΔS^*	=	entropy term in Eq. 24-4; evaluated with Eq. 24-5
T	=	temperature (K)
T_b	=	boiling point (K)
T_c	=	critical temperature (K)
T_r	=	reduced temperature = T/T_c
T_{rb}	=	reduced boiling point = T_b/T_c

Greek

- ρ_l = molar liquid density (mol/cm³)
 λ = thermal conductivity (cal/cm·s·K)
 λ_l = liquid thermal conductivity (cal/cm·s·K)

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25

DIPOLE MOMENT

Leslie H. Nelken and James D. Birkett

25-1 INTRODUCTION

Dipole moments result from electronegativity differences of the atoms within a molecule, electronegativity being defined by Pauling as the "power of an atom in a molecule to attract electrons to itself" [3]. A molecule becomes dipolar if the electrons forming the bond accumulate toward more electronegative atoms, leaving less electronegative atoms with a slight positive charge. The dipole moment, μ , can be defined as the vector in the direction of negative to positive charge of magnitude Qr , where Q is the charge and r is the charge separation distance. The unit of the dipole moment is the debye (D). One debye is equivalent to 10^{-18} electrostatic units-cm (esu-cm). For example, one positive and negative charge (4.8×10^{-19} esu/charge), separated by a distance of 0.1 nm (or 10^{-8} cm) would equal 4.8×10^{-18} esu-cm, or 4.8 debyes. Typically, dipole moments of organic molecules fall in the range of 0 to 5 debyes. Large molecules, such as dyes, may have a moment of up to 17 debyes [6].

Property correlations for polar compounds often require this parameter. For example, the boiling point of a chemical may be related to its heat of vaporization with a parameter (K_f) that may be derived from the dipole moment (see §14-3). This particular relationship is used in this handbook in one of the estimation methods for vapor pressure (see §14-3) and one for liquid viscosity (see §22-6). The dipole moment is also used in some pressure-volume-temperature relationships and in some estimation methods for the diffusion coefficients of polar gases.

The dipole moment is a fairly significant parameter used to aid in the determination of molecular structure, bond angles, and resonance. For instance, the fact that carbon dioxide has no dipole moment leads one to conclude the molecule is linear; water, on the other hand, cannot be linear, because it has a measured dipole moment. Both of these conclusions are in agreement with the structures predicted from molecular orbital considerations. The basis of light scattering in Raman spectroscopy is the dipole moment induced in the molecule when hit by the incident light beam [3]. Dipole moments are also responsible for the interaction of the molecules with radiation in the infrared and microwave regions, giving rise to their characteristic vibrational-rotational spectra. Lastly, the dipole moment is useful in ascertaining the potential for a molecule to interact with its surrounding medium via hydrogen bonding, Van der Waals forces, and dipole-dipole attractions [1]. (Van der Waals force differs from dipole-dipole attraction in that the former is an attraction between small, transient charges in molecules which are normally considered non-polar, whereas the latter involves permanent molecular dipoles [2].)

Dipole moments may be experimentally determined by a number of methods, including microwave spectroscopy, indices of refraction, infrared vibration/rotation spectra, and electron resonance. The most common method is based upon Debye's equation relating the dipole moment to the dielectric constant ¹ and temperature [3,8]:

$$\frac{(\epsilon-1)M}{(\epsilon+2)\rho} = \frac{4\pi N\alpha}{9\epsilon_0 kT} + \frac{4\pi N\mu^2}{9\epsilon_0 kT} \quad (25-1)$$

where

- ϵ = dielectric constant (dimensionless)
- ϵ_0 = dielectric constant of vacuum (dimensionless)
- M = molecular weight (g/mol)
- ρ = density (g/cm³)
- N = Avogadro's number, 6.02×10^{23} molecules/mole
- α = polarizability factor, or dipole induced by the electric field
- k = Boltzmann's constant, 1.3806×10^{-23} J/K
- T = temperature (K)

1. A dielectric is an insulating substance, and ϵ is the factor by which the dielectric increases the capacitance above that measured in a vacuum.

The dielectric constant, ϵ , can be calculated from the capacitance of a parallel-plate capacitor in which the dielectric is the vapor or solution between the plates [3]. A plot of the left-hand side of Eq. 25-1 versus $1/T$ over a wide temperature range will provide a slope (b) from which μ in the vapor or liquid state can be determined. LeFevre [2] has shown that when the constants are inserted into Eq. 25-1, the following equation is obtained:

$$\mu = 0.012816 \sqrt{b} \times 10^{-18} \quad (25-2)$$

There are two kinds of dipole moments — induced and permanent. The *induced* dipole, reflected by α in Eq. 25-1, is created by an electric field. Its value is temperature-independent, since the molecule will reorient itself in the direction of the field after it is perturbed by a thermally agitated molecule. The *permanent* dipole is caused by the electronegativity differences of the atoms within the molecule and is temperature-dependent. At higher temperatures, the random movement of molecules opposes their tendency to become oriented in the direction of the electric field.

Equation 25-1 applies most accurately to gases when the pressure is low enough so that the gas molecules have little opportunity to interact. However, measurement of μ (or ϵ) in the gaseous state is a difficult procedure, so the measurement is often made with the molecule in the liquid state. Measurement of ϵ in the liquid state is affected by the forces exerted by the closely packed molecules upon each other, and by the solvent interacting with the molecules of interest. The effects of solvation may be minimized by measuring ϵ in a dilute solution in which the solvent is a non-polar organic liquid such as benzene or carbon tetrachloride.

25-2 AVAILABLE ESTIMATION METHODS

The most accurate methods for estimating dipole moments require a knowledge of the bond angles between atoms. Only a few such methods have been developed, and their complexity makes them unsuitable for inclusion in this handbook. Readers who desire further details should refer to Smyth's comprehensive dissertation on this subject [6].

The dipole moment may also be calculated with a computer program, CAMSEQ, which performs a variety of calculations related to molecular mechanics and molecular structure [4]. The heart of this program involves the calculation of conformational potential energy for

selected molecular conformations until a structure of minimum energy is found. Various properties of the molecule are then calculated for the preferred structure. A significant amount of computer time is required to carry out this analysis.

Dipole moments of certain molecular structures can be closely estimated without resorting to large-scale computations. Fishtine [1] developed a fairly easy method for calculating the dipole moment of substituted benzenes, naphthalene derivatives, and heterocyclics containing nitrogen, oxygen, and sulfur. Unfortunately, similar methods are not available for aliphatic and alicyclic compounds. Table 25-1 lists the average values (\bar{x}) of experimentally determined dipole moments for about 20 chemical classes of aliphatic and alicyclic liquids and vapors and also shows the standard deviations (σ) from the average. Most dipole moments fall in the range of 0 to 5 debye units.

25-3 ESTIMATION OF DIPOLE MOMENTS FOR AROMATIC COMPOUNDS

Fishtine [1] describes methods for calculating the dipole moment of substituted benzenes, naphthalenes, and heterocyclic compounds such as pyridine, furan, and thiophene. Excluded from this group are substituents that participate in hydrogen bonding, such as phenols and anilines. The steps in the calculation differ for each class of compound. There are three sub-categories of substituted benzenes to reflect variations in the symmetry of the substituents.²

Table 25-2 lists the dipole moment contributions (compiled by Smyth [6]) of about 30 substituents to benzene rings, including halogens, cyanides, sulfide groups, methyl esters, and cyanates. These are grouped according to the direction in which the dipole points (i.e., the location of the negative end of the dipole). Asymmetrical substituents are designated by an "x" in the third column.

The dipole moment was calculated for a sample group of aromatic compounds (Table 25-3) to find the absolute error associated with this method. Most errors were in the 2-30% range. From the small group of compounds tested, it is not possible to determine the chemical classes for which the method will yield poor results and why.

2. "Symmetry" in this case refers to that of the atoms that comprise the substituent rather than the arrangement of substituents around the benzene ring.

TABLE 25-1

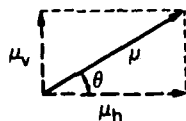
Typical Values of Experimentally Determined
Dipole Moments of Aliphatic and Alicyclic Chemicals

Chemical Class	Liquids			Vapors		
	n	\bar{x}	σ	n	\bar{x}	σ
Paraffins	4	0	0.0	7	0	0.0
Saturated cyclic hydrocarbons	8	0	0.0	4	0	0.0
Mono/di-alkenes				15	0.4	0.3
Alkyl acetylenes				7	0.6	0.4
Alkyl halides				20	2.0	0.1
Polyhalogenated alkanes	15	1.35	0.7	26	1.1	0.8
Halogenated cyclic alkanes	28	1.68	1.6			
Halogenated alkenes	21	1.1	0.7	12	1.6	0.5
Halogenated alkynes	9	0.8	0.4			
Cyanogens, HCN, substituted cyanides	6	2.9	0.7	3	1.9	1.6
Alkyl, cyclic, and unsaturated cyanides	11	3.7	0.2	8	4.0	0.2
Isocyanides, isocyanates, thiocyanates, isothiocyanates	7	3.3	0.3			
Nitroalkanes, chloronitroalkanes	9	2.7	1.1	11	3.0	1.1
Aldehydes	15	2.6	0.5	7	2.8	0.4
Ketones	42	2.7	0.7			
Ethers	11	1.3	0.3	5	1.2	0.1
Alicyclic oxides	21	1.6	0.6			
Alcohols	8	1.6	0.0	6	1.7	0.0
Sulfides/mercaptans	13	1.4	0.3	6	1.3	0.4
Monocarboxylic acids, esters	34	1.9	0.2			
Amines	10	1.2	0.2			
Fulvenes and azulene	10	1.2	0.3			

n = no. of compounds; \bar{x} = avg. value (debyes); σ = std. deviation (debyes)

Source: Smyth [6]

Calculation of the dipole moment by this method entails the addition of vectors lying in the same plane. Each substituent dipole moment (μ) can be considered to have a vertical component (μ_v) and a horizontal component (μ_h):



$$\mu_v = \mu \sin \theta \quad (25-3)$$

$$\mu_h = \mu \cos \theta \quad (25-4)$$

TABLE 25-2

Magnitude and Direction of
Electrical Moments of Benzene Derivatives

Group A in C_6H_5-A	Dipole Moment of C_6H_5-A	Substituent is Asymmetric	Vector Points:
-H	0.0		
-CH=CH ₂	a		
-CH ₃	0.4		Toward Ring
-C ₂ H ₅	0.4	x	
-CH(CH ₃) ₂	0.6	x	
-C(CH ₃) ₃	0.5		
-N(CH ₃) ₂	1.57	x	
-F	1.46		Away from Ring
-Cl	1.58		
-Br	1.54		
-I	1.30		
-CH ₂ Cl	1.85	x	
-CHCl ₂	2.04	x	
-CCl ₃	2.11		
-CH ₂ Br	1.86	x	
-CN	3.90		
-CH ₂ CN	3.5	x	
-NC	3.5		
-NCO	2.32		
-SCN thiocyanate	3.59		
-NCS isothiocyanate	2.9		
-NO ₂	3.98		
-CH ₂ NO ₂	3.3	x	
-NO	3.14		
-CHO	2.76	x	
-COCH ₃	2.89	x	
-OCH ₃	1.25	x	
-SCH ₃	1.3	x	
-OH	1.6	x	
-SH	1.3	x	
-COOCH ₃	1.83	x	

a. Small, but greater than zero.

Source: Fishline [1]

TABLE 25-3

Comparison of Observed and Estimated Dipole Moments

Compound	Dipole Moment, μ (debyes)		Error (%)
	Observed ^a	Estimated ^b	
<i>p</i> -Bromophenoxy- <i>p</i> -toluene	2.45	2.30	- 6
<i>p</i> -Nitrophenoxybenzene	4.54	3.5	-23
<i>m</i> -Nitromethoxybenzene	4.55	3.5	-23
<i>o</i> -Fluorotoluene	1.86	1.7	- 9
<i>o</i> -Chloro (trifluoromethyl) benzene	3.46	3.2	- 7
<i>m</i> -Difluorobenzene	1.58	1.5	- 5
2,3,4,5-Tetrabromothiophene	0.73	0.5	-26
2-Mercaptobenzothiazole	4.0	2.4	-40
4-Methoxypyridine	2.94	1.9	-34
2,7-Dichloronaphthalene	1.53	1.2	-21
1-Bromo-5-nitronaphthalene	2.49	2.4	- 2
<i>p</i> -Nitrobiphenyl	4.22	4.0	- 5
1,2,3,4-Tetramethyldinitrobenzene	6.86	7.6	+10
1,2-Dimethyl-3,4,5-trichlorobenzene	2.46	3.7	+50
<i>m</i> -Chloronitrobenzene	3.40	3.5	+ 2
<i>p</i> -Bromobenzaldehyde	2.20	2.4	+ 9
<i>p</i> -Benzenedicarboxaldehyde	2.35	2.8	+17
Average Absolute Error			17%
Standard Deviation			14.1%

a. As reported by Smyth [6]

b. Calculated from substituent moments listed in Table 25-2.

The magnitude of these components can be calculated by Eqs. 25-3 and -4 from μ and the angle (θ) of the substituent vector from horizontal. Just as a point may be represented in Cartesian coordinates as (x,y), we may represent the substituent vector as (μ_h , μ_v). The sum of two vectors (1 and 2) is, in this manner, represented by the sum of their individual horizontal and vertical components, i.e., ($\mu_{h_1} + \mu_{h_2}$, $\mu_{v_1} + \mu_{v_2}$). Vector components that point in the positive direction of the selected coordinates are positive, and those that point in the negative direction are negative. In Cartesian coordinates, positive signs are normally associated with the "up" direction (μ values above the abscissa) and with the "right" direction (x values to the right of the ordinate). Thus, in the diagram above, both μ_v and μ_h would be positive; if μ had pointed in the opposite direction, both μ_v and μ_h would be negative.

The length of any vector expressed by its vertical and horizontal components, μ_v and μ_h , is

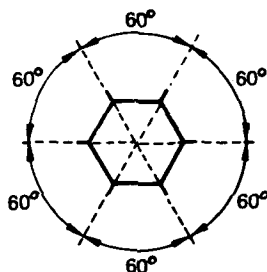
$$\mu = \sqrt{\mu_v^2 + \mu_h^2} \quad (25-5)$$

When this vector is the sum of several vectors,

$$\mu = \left[\left(\sum_{i=1}^n \mu_{v_i} \right)^2 + \left(\sum_{i=1}^n \mu_{h_i} \right)^2 \right]^{1/2} \quad (25-6)$$

where the individual values of μ_{v_i} and μ_{h_i} for the n substituents on the benzene ring are the values obtained from Eqs. 25-3 and -4, respectively.

The angles of the benzene-substituent bonds are individually separated by 60° , as shown below.



Thus, if one substituent position is set at $\theta = 0^\circ$, the θ for any other substituent must be some multiple of 60° . The signs (+ or -) of the μ_v and μ_h values are automatically calculated if θ is always measured from the same reference line (e.g., the positive direction of the abscissa) and in the same direction (e.g., counterclockwise) around to the direction in which the substituent dipole is pointing. These directions are either directly toward or away from the center of the benzene ring (see Table 25-2).

An easy way to obtain the correct θ for each substituent is to draw the basic benzene structure with arrows at each substituent location pointing in the correct direction. Then transfer the arrows to a diagram where the tails of all arrows start at a common point. Finally, measure the θ angles by moving counterclockwise from the positive abscissa direction. Examples are given in Figure 25-1.

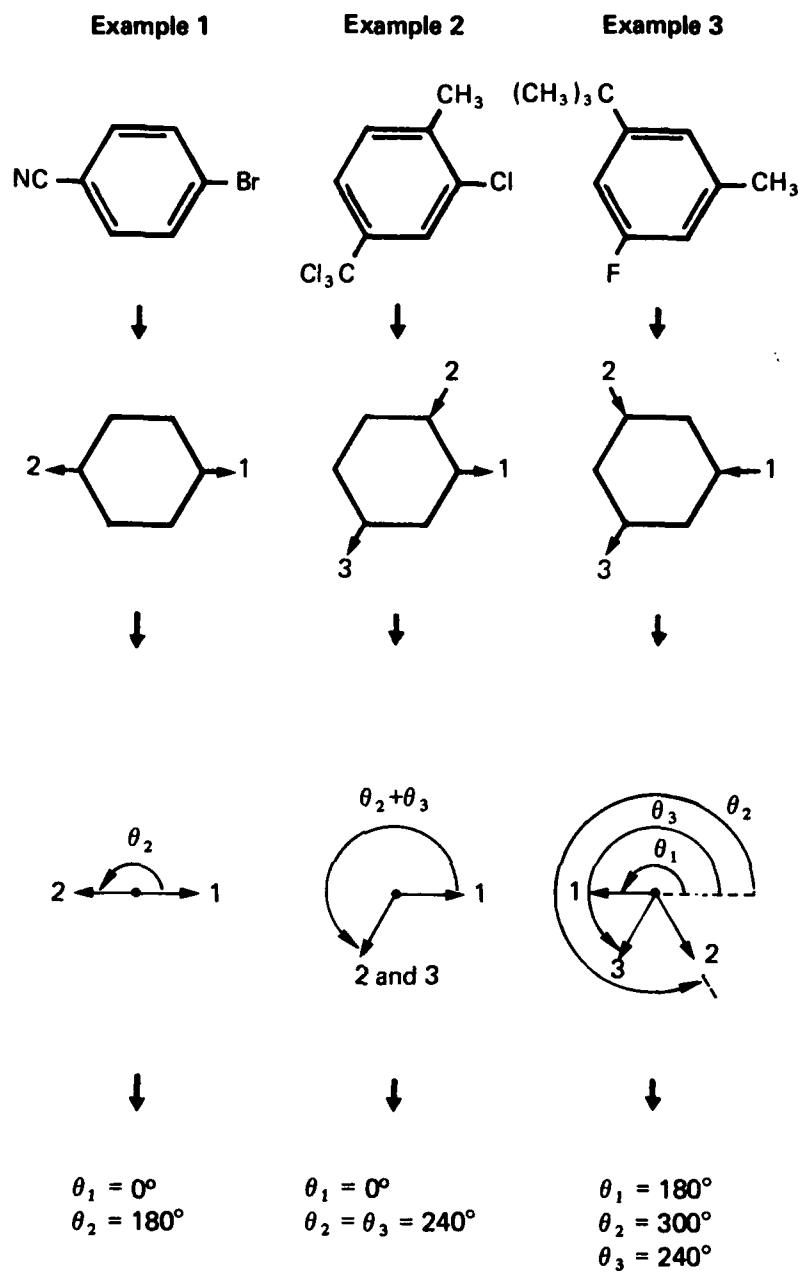


FIGURE 25-1 Examples of the Determination of θ

The method is described in more detail below for four different classes of compounds:

- (1) Substituted benzenes with no hydrogen bonding
 - Symmetrical functional groups
 - One asymmetrical functional group
 - More than one asymmetrical functional group
- (2) Naphthalene derivatives
- (3) Heterocyclics
- (4) Miscellaneous compounds

Substituted Benzenes with No Hydrogen Bonding

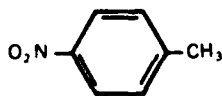
• *Symmetrical Functional Groups.* Addition of symmetrical functional groups on the benzene ring is a case of straightforward vector addition.

Basic Steps

- (1) Draw the chemical structure.
- (2) Obtain the dipole moment of each substituent (μ) from Table 25-2. Note the direction of the dipole moment as indicated by the direction of the arrow in the right-hand column of the table.
- (3) Draw a benzene ring with an arrow at each substituent position pointing in the direction indicated by Step 2. (See Figure 25-1 for examples.) Then determine the angle, θ , for each substituent vector (arrow).
- (4) Calculate the vertical and horizontal components of each substituent dipole (μ_v and μ_h) using Eqs. 25-3 and -4.
- (5) Calculate the resulting dipole for the whole molecule, μ , from Eq. 25-6. The answer is in units of debyes.

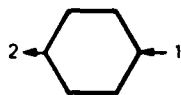
Example 25-1 Estimate the dipole moment of p-nitrotoluene.

- (1) The structure is

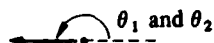


- (2) From Table 25-2, the substituent dipoles (μ) for $-\text{CH}_3$ and $\text{O}_2\text{N}-$ are 0.4 and 3.98, respectively. Table 25-2 indicates an arrow pointing toward the ring for $-\text{CH}_3$ and away from the ring for $\text{O}_2\text{N}-$.

- (3) The vectors are represented as:



θ is 180° for both vectors 1 and 2



- (4) The vertical components (μ_v) of both vectors are 0, since $\sin(180^\circ) = 0$. The horizontal components (Eq. 25-4) are

$$\mu_h (\text{O}_2\text{N}-) = 3.98 \cos(180^\circ) = 3.98 (-1) = -3.98$$

$$\mu_h (-\text{CH}_3) = 0.4 \cos(180^\circ) = 0.4 (-1) = -0.4$$

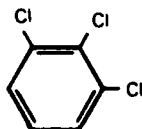
- (5) The resulting dipole for the molecule, from Eq. 25-6, is

$$\mu = \sqrt{(-0.4 - 3.98)^2} = 4.4 \text{ D}$$

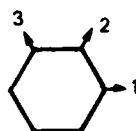
The measured value is also 4.4 D [1].

Example 25-2 Estimate the dipole moment of 1,2,3-trichlorobenzene

- (1) The structure is



- (2) From Table 25-2, the substituent dipole (μ) for $-\text{Cl}$ is 1.58 and the vector points away from the ring.
 (3) The benzene vector diagram is:



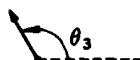
θ for vector 1 is 360° or 0° :



θ for vector 2 is 60°



θ for vector 3 is 120°



- (4) The vertical component of each vector is:

$$\begin{aligned}\mu_v(1) &= 1.58 \sin(0^\circ) = 0 \\ \mu_v(2) &= 1.58 \sin(60^\circ) = 1.37 \\ \mu_v(3) &= 1.58 \sin(120^\circ) = 1.37\end{aligned}$$

The horizontal component of each vector is:

$$\begin{aligned}\mu_h(1) &= 1.58 \cos(0^\circ) = 1.58 \\ \mu_h(2) &= 1.58 \cos(60^\circ) = 0.79 \\ \mu_h(3) &= 1.58 \cos(120^\circ) = -0.79\end{aligned}$$

- (5) The resulting dipole for the molecule, from Eq. 25-6, is

$$\mu = \sqrt{[0 + 2(1.37)]^2 + (1.58 + 0.79 - 0.79)^2} = 3.16 \text{ D}$$

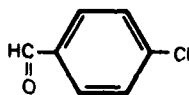
The measured value is 2.31 [1], giving a deviation of 37%.

• One Asymmetrical Functional Group

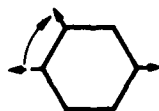
Basic Steps. The calculation of μ is the same as in the case of symmetrical functional groups, except that if the asymmetrical substituent is in the para position, its horizontal and vertical components should be calculated as though it were in the meta position.

Example 25-3 Estimate the dipole moment of p-chlorobenzaldehyde.

- (1) The structure is



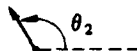
- (2) From Table 25-2, the substituent dipole (μ) is 1.58 for $-\text{Cl}$ and 2.76 for $-\text{CHO}$. The table shows that $-\text{CHO}$ is asymmetrical and that both dipoles point away from the ring.
- (3) The benzene vector diagram is as follows (the asymmetrical $-\text{CHO}$ group is treated as though it were in a position meta to the symmetrical Cl group):



θ for Cl is 0° :



θ for $-\text{CHO}$ is 120° :



- (4) The vertical component of each vector is:

$$\mu_v(-\text{Cl}) = 1.58 \sin(0^\circ) = 0$$

$$\mu_v(-\text{CHO}) = 2.76 \sin(120^\circ) = 2.39$$

The horizontal components are:

$$\mu_h(-\text{Cl}) = 1.58 \cos(0^\circ) = 1.58$$

$$\mu_h(-\text{CHO}) = 2.76 \cos(120^\circ) = -1.38$$

- (5) From Eq. 25-6, the resulting dipole for the molecule is

$$\mu = \sqrt{(2.39)^2 + (1.58 - 1.38)^2} = 2.40$$

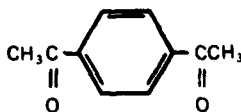
The experimental value is 2.03 [1]; the deviation is +18%.

• More Than One Asymmetrical Functional Group

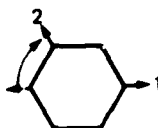
Basic Steps. If the asymmetrical groups are ortho or meta to each other, the calculation of μ is the same as for symmetrical functional groups. If they are para to each other, perform the calculation as though one group were shifted to the meta position, such that the maximum moment for the compound is achieved.

Example 25-4 Estimate the dipole moment of p-acetylacetophenone.

- (1) The structure is:



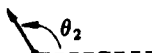
- (2) From Table 25-2, the substituent dipole value for $-\text{COCH}_3$ is 2.89. The substituent is asymmetrical, and its vector points away from the ring.
- (3) The benzene vector diagram is drawn as though one $-\text{COCH}_3$ is moved to a position meta to the other:



θ for vector 1 is 0° :



θ for vector 2 is 120° :



- (4) The vertical component of each vector is:

$$\mu_v (\text{CH}_3\text{CO})_1 = 2.89 \sin (0^\circ) = 0$$

$$\mu_v (\text{CH}_3\text{CO})_2 = 2.89 \sin (120^\circ) = 2.50$$

The horizontal component is:

$$\mu_h (\text{CH}_3\text{CO})_1 = 2.89 \cos (0^\circ) = 2.89$$

$$\mu_h (\text{CH}_3\text{CO})_2 = 2.89 \cos (120^\circ) = -1.44$$

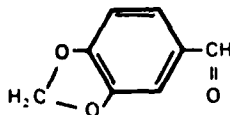
- (5) From Eq. 25-6, the resulting dipole for the molecule is:

$$\mu = \sqrt{(2.50)^2 + (2.89 - 1.44)^2} = 2.89$$

The experimental value is 2.71 [1], indicating a + 7% error.

Example 25-5 Estimate the dipole moment of piperonal.

- (1) The structure is:



- (2) Since the μ value of the cyclic ether substituent is not listed in Table 25-2, replace it with two separate substituents with known dipole moments. The $-\text{OCH}_3$ group is the most appropriate candidate.
- (3) The molecule is now assumed to have one $-\text{CHO}$ substituent ($\mu = 2.76$) and two $-\text{OCH}_3$ substituents ($\mu = 1.25$). All of these are asymmetrical, and their vectors point away from the ring.
- (4) Since two asymmetrical groups lie para to each other, the benzene vector diagram is modified as follows:



The vector angles are 180° , 240° , and 300° from the horizontal.

The other option would be to move the $p\text{-OCH}_3$ group to a position meta to the CHO group. This option is discounted since it will not result in a maximum dipole for the compound.

- (5) The vertical component of each vector is:

$$\mu_v(-\text{CHO}) = 2.76 \sin(300^\circ) = -2.39$$

$$\mu_v(-\text{OCH}_3)_1 = 1.25 \sin(240^\circ) = -1.08$$

$$\mu_v(-\text{OCH}_3)_2 = 1.25 \sin(180^\circ) = 0$$

The horizontal component of each vector is:

$$\mu_h(-\text{CHO}) = 2.76 \cos(300^\circ) = -1.38$$

$$\mu_h(-\text{OCH}_3)_1 = 1.25 \cos(240^\circ) = -0.625$$

$$\mu_h(-\text{OCH}_3)_2 = 1.25 \cos(180^\circ) = -1.25$$

- (6) From Eq. 25-6, the resulting dipole for the molecule is:

$$\mu = \sqrt{(-2.39 - 1.08)^2 + (1.38 - 0.625 - 1.25)^2} = 3.50$$

No value for piperonal was found in the literature.

Naphthalene Derivatives. For estimation purposes, assume the naphthalene molecule to be octagonal, making the angle between two adjacent substituents 45° . Use Table 25-2 for the moments of substituent groups and apply the rules for symmetrical substituents given in the preceding section.

Basic Steps

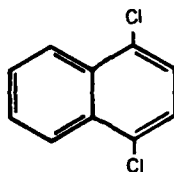
- (1) Draw the chemical structure.
- (2) Obtain the dipole moment of each substituent, μ , from Table 25-2. Note the direction of the dipole moment indicated in the right-hand column.
- (3) Draw the naphthalene structure with vectors at each substituent position in the direction found in Step 2. Then transform the structure into an octagon (representing the

eight possible points of attachment in naphthalene), with the x-axis passing through the middle of the vertical sides. Determine the angle, θ , for each substituent by moving counterclockwise from 0° .

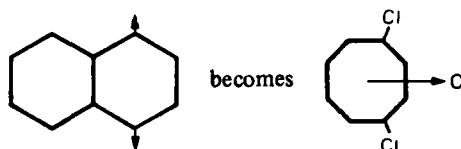
- (4) Calculate the vertical and horizontal components of each vector (μ_v and μ_h) using Eqs. 25-3 and -4.
- (5) Calculate the resulting dipole for the whole molecule, μ , from Eq. 25-6.

Example 25-6 Calculate the dipole moment of 1,4-dichloronaphthalene.

- (1) The structure is



- (2) From Table 25-2, the substituent dipole value of $-Cl$ is 1.58. The substituent is symmetrical, and its vector points away from the ring.
- (3) The naphthalene vector diagram develops as follows:



The vector angles are 67.5° and 292.5° from the horizontal:



- (4) The vertical components of the vectors are:

$$\mu_v (Cl_1) = 1.58 \sin (67.5^\circ) = 1.46$$

$$\mu_v (Cl_2) = 1.58 \sin (292.5^\circ) = -1.46$$

The horizontal component of the vector is:

$$\mu_h (Cl_1) = 1.58 \cos (67.5^\circ) = 0.60$$

$$\mu_h (Cl_2) = 1.58 \cos (292.5^\circ) = 0.60$$

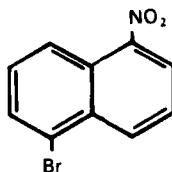
- (5) The resultant dipole moment (Eq. 25-6) is

$$\mu = \sqrt{(1.46 - 1.46)^2 + (0.60 + 0.60)^2} = 1.2$$

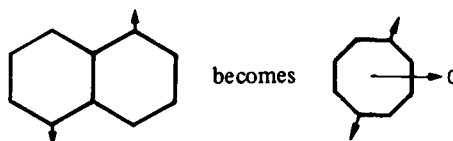
The measured value of the dipole is 0.48 [6], indicating a large error of 152%.
The measured dipole of 1,5-dichloronaphthalene is 1.78. Obviously, the angle approximation of 45° in the molecule contributes to the error.

Example 25-7 Estimate the dipole moment for 1,5-bromonitronaphthalene.

- (1) The structure is



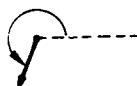
- (2) The substituent values for $-\text{Br}$ and $-\text{NO}_2$ from Table 25-2 are 1.54 and 3.98, respectively, and both dipoles point away from the ring.
(3) The naphthalene vector diagram appears as follows:



The vector angle for $-\text{NO}_2$ is 67.5°



The vector angle for $-\text{Br}$ (247.5°) appears as



- (4) The vertical component of the vector is:

$$\mu_v (-\text{NO}_2) = 3.98 \sin (67.5^\circ) = 3.68$$

$$\mu_v (-\text{Br}) = 1.54 \sin (247.5^\circ) = -1.42$$

The horizontal component is

$$\mu_h (-\text{NO}_2) = 3.98 \cos (67.5^\circ) = 1.52$$

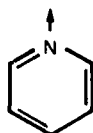
$$\mu_h (-\text{Br}) = 1.54 \cos (247.5^\circ) = -0.59$$

- (5) From Eq. 25-6, the calculated dipole moment is

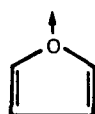
$$\mu = \sqrt{(3.68 - 1.42)^2 + (1.52 - 0.59)^2} = 2.44$$

Smythe [6] reports a measured value of 2.49, indicating an error of -2.0%.

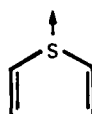
Heterocyclics. The dipole vector diagrams for pyridine, furan, and thiophene are illustrated below. The arrow indicates that for all three heterocyclics, the positive end of the dipole is at the ring. For five-membered rings, assume that the bond angles are 60° , as for six-membered rings [1].



$$\mu = 2.23$$



$$\mu = 0.69$$

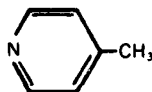


$$\mu = 0.54$$

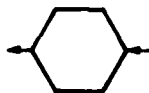
Basic Steps. Follow the sequence of steps outlined for symmetrical functional groups on benzene. The only difference is that the parent molecule possesses a dipole moment.

Example 25-8 Estimate the dipole moment of 4-methylpyridine.

- (1) The structure is:



- (2) Table 25-2 indicates the substituent value of $-\text{CH}_3$ is 0.4, pointing toward the ring. The dipole value of pyridine is 2.23, pointing away from the ring.
- (3) The pyridine vector diagram is



θ is 180° for both vectors.

- (4) The vertical component, μ_v , of both vectors is 0, since $\sin 180^\circ = 0$. The horizontal components, from Eq. 25-4, are:

$$\mu_h (-\text{CH}_3) = 0.4 \cos (180^\circ) = -0.4$$

$$\mu_h (\text{pyridine}) = 2.23 \cos (180^\circ) = -2.23$$

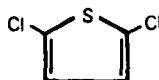
- (5) The resulting dipole for the molecule, from Eq. 25-6, is

$$\mu = \sqrt{(0)^2 + (-0.4 - 2.23)^2} = 2.63$$

The observed value is 2.57 [6], indicating a +2.3% error.

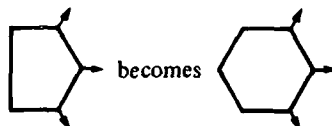
Example 25-9 Estimate the dipole moment of 2,5-dichlorothiophene.

- (1) The structure is:



- (2) Table 25-2 lists the substituent value of -Cl as 1.58. All dipole vectors point away from the ring.

- (3) The thiophene diagram is:



- (4) The vector angles are 60° and 300° for the -Cl substituents and 0° for thiophene.

The vertical components of the vectors are:

$$\mu_v (-\text{Cl})_1 = 1.58 \sin 60^\circ = 1.37$$

$$\mu_v (\text{thiophene}) = 0.54 \sin 0^\circ = 0$$

$$\mu_v (-\text{Cl})_2 = 1.58 \sin 300^\circ = -1.37$$

The horizontal components are:

$$\mu_h (-\text{Cl})_1 = 1.58 \cos 60^\circ = 0.79$$

$$\mu_h (\text{thiophene}) = 0.54 \cos 0^\circ = 0.54$$

$$\mu_h (-\text{Cl})_2 = 1.58 \cos 300^\circ = 0.79$$

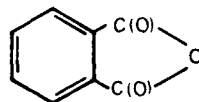
- (5) The resulting dipole moment from Eq. 25-6 is

$$\mu = \sqrt{(1.37 + 0 - 1.37)^2 + (0.79 + 0.54 + 0.79)^2} = 2.12$$

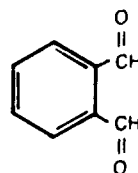
The value reported in the literature is 1.12 [6], indicating a large (89%) error.

Miscellaneous Compounds. Calculation of μ by this method requires judgment on the part of the user. Fishtine [1] presents a few cases (e.g., Example 25-5) where the procedure was not strictly circumscribed. Another example is salicylaldehyde (o-hydroxybenzaldehyde): typically, this molecule would be excluded from the estimation technique, since the -OH substituent could participate in hydrogen bonding. Knowledge of the chemistry of this molecule, however, would permit evaluation of μ , since the -OH participates in *intramolecular* hydrogen bonding and thus cannot interact in *intermolecular* hydrogen bonding.

A third example requiring judgment on the part of the user is estimation of μ for phthalic anhydrides:



Fishtine suggests converting the molecule to



for which the information necessary to calculate μ exists.

25-4 AVAILABLE DATA

Values for dipole moments are given by Smyth [6] and in the following two books referenced by Reid *et al.* [5]:

McClellan, A.L., *Tables of Experimental Dipole Moments*, Freeman, San Francisco (1963).

Minkin, V.I., O.A. Osipov and Y.A. Zhdanov, *Dipole Moments in Organic Chemistry*, translated from Russian by B.J. Hazard, Plenum Press, New York (1970).

Another source is:

Gordon, A.J. and R.A. Ford, *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, John Wiley and Sons, New York (1972).

The dipole moments of a few compounds are listed in Ref. 7 and in other sources listed in Appendix A.

25-5 SYMBOLS USED

b	=	parameter in Eq. 25-2
k	=	Boltzmann's constant in Eq. 25-1
M	=	molecular weight in Eq. 25-1 (g/mol)
N	=	Avogadro's number in Eq. 25-1
n	=	number of samples
Q	=	charge on one electron ($= 4.8 \times 10^{-10}$ esu)
r	=	distance of charge separation (cm)
T	=	temperature in Eq. 25-1 (K)
\bar{x}	=	average of n values
x	=	abscissa component of vector
y	=	ordinate component of vector

Greek

α	=	polarity in Eq. 25-1
ϵ	=	dielectric constant in Eq. 25-1
μ	=	dipole moment in Eq. 25-1 (debye)
ρ	=	density in Eq. 25-1 (g/cm ³)
σ	=	standard deviation
θ	=	angle of substituent vector from horizontal (see Fig. 25-1)

Subscripts

h	=	horizontal component of vector
v	=	vertical component of vector

25-6 REFERENCES

1. Fishtine, S.H., "Reliable Latent Heats of Vaporization," *Ind. Eng. Chem.*, 55 (6), 47-56 (1963).
2. LeFevre, R.J.W., *Dipole Moments, Their Measurement and Application in Chemistry*, John Wiley and Sons, New York (1953).
3. Moore, W.J., *Physical Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, N.J. (1972).
4. Potenzzone, R., Jr., E. Cavicchi, H.J.R. Weintraub and A.J. Hopfinger, "Molecular Mechanics and the CAMSEQ Processor," *Comput. Chem.*, 1, 187-94 (1977).

5. Reid, R.C., J.M. Prausnitz, and T.K. Sherwood, *The Properties of Gases and Liquids*, 3rd. ed., McGraw-Hill Book Co., New York (1977).
6. Smyth, C.P., *Dielectric Behavior and Structure*, McGraw-Hill Book Co., New York (1956).
7. Weast, R.C. (ed.), *Handbook of Chemistry and Physics*, 59th ed., Chemical Rubber Co., Cleveland, Ohio (1979-80).
8. Wheatley, P.J., *The Determination of Molecular Structure*, Oxford University Press, London (1959).

26

INDEX OF REFRACTION

Leslie H. Nelken

26-1 INTRODUCTION

The index of refraction (n) and molar refraction (R_D) are indications of the manner in which a molecule interacts with light. The index of refraction is the ratio of the speed of light in a vacuum (c) to the speed of light in the medium (v):

$$n = c/v \quad (26-1)$$

This is a dimensionless parameter which ranges between 1.3 and 1.5 for organic liquids. (See, for example, Ref. 15.)

The refractive index is measured using a beam of monochromatic light — typically, the yellow light of the sodium D line (wavelength $\lambda = 589.3$ nm). Thus, n_D^{20} indicates the wavelength used, D, and the temperature, 20°C. Other wavelengths used are the C and F lines of hydrogen ($\lambda = 656.3$ nm and 486.1 nm, respectively) and the G line of mercury ($\lambda = 435.8$ nm) [12].

Molar refraction, R_D , is a function of the density, ρ , of the medium. The Lorentz-Lorenz equation (26-2) expresses the relationship between R_D , ρ , and n , based upon electromagnetic theory:

$$R_D = \left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{M}{\rho} \quad (26-2)$$

where M is molecular weight and R_D has units of volume. (A term related to R_D is the specific refraction, which equals R_D divided by M .) Rearrangement of Eq. 26-2 allows evaluation of n :

$$n = \sqrt{\frac{M + 2\rho R_D}{M - \rho R_D}} \quad (26-3)$$

Molar refraction and refractive indices have many uses. They are often required in confirming the identity and purity of a compound. Determination of molecular structure and weight is often aided by these parameters [6]. R_D is also used in other estimation schemes, such as in critical properties [9], surface tension [11], and the solubility parameter, which is a measure of intermolecular forces [8].

The refractive index, n , is affected by changes in temperature, pressure, and wavelength of radiation. (R_D remains nearly constant with changes of temperature and pressure by virtue of the density factor, which is a function of temperature and pressure and, thus, offsets these effects.) Methods for extrapolating values of n from one temperature to another are provided in § 26-7.

The refractive index increases as pressure increases, due to the resulting increase in density. This effect is not as significant with liquids as with gases [12]. Lastly, the refractive index decreases as the wavelength increases. For this reason, one cannot compare indices measured at different wavelengths of light [12].

26-2 AVAILABLE ESTIMATION METHODS

Group Contribution Methods. Only two types of methods are available for estimating n or R_D . The first of these is additive in nature. The earliest method of this kind was developed by Eisenlohr [1] in 1910 and subsequently published by Ward and Kurtz [15], Meissner [9], Reid and Sherwood [11], and Gold and Ogle [2]. The method relies upon atomic and structural contributions to estimate R_D . The density and molecular weight are then required to calculate a value of n . The error in R_D is usually less than $\pm 5\%$ but can be as much as 10% for two specific classes of compounds [2]:

- The calculated R_D for a compound containing conjugated double bonds is always less than the observed value. For polynuclear aromatics, the discrepancy can be large.

- The calculated R_D for furan-type compounds is always greater than the observed value.

Vogel developed two group contribution methods. By one of these [13], the molar refractivity and index of refraction for the sodium D line at 20°C can be calculated by adding atomic, structural, and group contributions; by the other [14], the parameters are found by adding bond refractions at 20°C. Vogel's group contribution method may handle a more diverse set of chemical classes: unlike that of Eisenlohr, it can be used for phosphates, sulfites, sulfates, nitro compounds, nitrates, and carbonates.

Hansch *et al.* [4] applied the group contributions for R_D tabulated by Vogel to an even larger variety of aromatic substituents. These values were collected to study the quantitative relationships between structure and activity in biochemical/biomedical systems. For very complex aromatics, use of the group contributions collected by Hansch *et al.* should provide a good estimate of the molar refraction.

Connectivity Method. The other general method for computing molar refraction is also based upon molecular structure but involves the use of a connectivity function, χ , developed by Kier and Hall [5]. This function can be correlated with R_D by regression equations, which presently exist for the following groups of chemical classes: alcohols, ethers, amines, halogen-containing saturated compounds, alkanes, substituted alkyl benzenes, and mono-olefinic alkenes. The correlation coefficient is generally near 0.99 [5]. Although this method is quite accurate, hand computation of χ is time-consuming. A computer program has been developed by Kier [3] for calculating χ , which greatly improves the likelihood that the connectivity method will be applied to more chemical classes and even adapted to many estimation methods besides that for R_D . For the present, however, the additive methods provide a simple and accurate alternative.

26-3 SELECTION OF APPROPRIATE METHOD

Recommended Methods. Table 26-1 summarizes the estimation methods recommended in this chapter. The methods of Eisenlohr and Vogel require only structural information to estimate R_D , and both require the molecular weight and density for the subsequent calculation of n . Furthermore, both methods use atomic and fragment constants to

TABLE 26-1

Overview of Recommended Methods

Method	Information Required	Applicability	Method Error ^a
Eisenlohr [1] (§ 26-4)	Structure only for R_D . ρ needed to calculate n .	Compounds with C, H,O,N,S,F, Cl, Br, I; double or triple bonds; aromatics	~ 1.6% ^b
Vogel [13, 14] (§ 26-5)	Structure only for R_D (ρ needed to calculate n from R_D). n (at 20°C) may also be calculated directly from structural information.	As above, plus phos- phates, sulfites, sulfates, nitrates and carbonates	~ 1.1%
Hansch, et al. [4] (§ 26-6)	Structure only for R_D . ρ needed to calculate n .	Substituted benzenes	~ 0.7%

a. Percentage errors apply to R_D and are the averages from the test sets in Tables 26-2 and 26-3. A 1% error in R_D typically translates into an error of ~0.3% in n . A 5% error in R_D (about the maximum observed) translates into a 1-2% error in n .

b. See § 26-4 for additional information.

calculate R_D and appear to involve about the same method error. Vogel's method is applicable to a somewhat larger number of chemicals. The third method, that of Hansch *et al.*, is only for substituted benzene compounds.

Method Errors. Table 26-2 compares the values and errors resulting from estimating molar refraction by Eisenlohr's and Vogel's group contribution methods. The average absolute error achieved by Eisenlohr's group contributions is 1.6%; for Vogel's method, the error is 1.1%. Both methods achieved the same approximation range or error for the separate chemical classes. Additional information, given in § 26-4 below, indicates that a method error of 0.2-0.3% may be expected for some chemical classes with Eisenlohr's method.

Table 26-3 similarly indicates the error resulting from estimating R_D by Hansch's method. The error attributable to this method was not evident in the literature, and the value generated in Table 26-3 is not

TABLE 26-2

Comparison of Observed Molar Refraction with Values Estimated by
Methods of Eisenlohr and Vogel

	Observed ^b R _D (cm ³)	Eisenlohr		Vogel	
		Estimated R _D (cm ³)	Error (%)	Estimated R _D (cm ³)	Error (%)
Hydrocarbons					
4-Methylheptane	39.12	39.14	+0.1	39.12	0
2,4-Dimethyl-3-isopropylpentane	47.91	48.38	+1.0	48.39	+1.0
3,3-Diethylpentane	43.12	43.76	+1.5	43.79	+1.5
1-Methyl-3-propylbenzene	45.36	44.78	-1.3	44.80	-1.2
1-Isopropyl-2-methylbenzene	45.09	44.78	-0.7	43.20	-4.2
sec-Butylbenzene	45.04	44.78	-0.6	44.78	-0.6
O-Containing Compounds					
1,1-Dimethyl-3-propanol	26.70	28.81	+7.9	26.76	+0.2
1,1,3,3-Tetramethyl-2-propanol	35.67	36.05	+1.0	36.05	+1.1
4-Ethyl-4-heptanol	44.92	45.29	+0.8	45.30	+0.8
Triethylene glycol monobutyl ether	54.85	54.83	0	55.31	+0.8
1,2-Dimethoxyethane	24.17	23.96	-0.9	24.13	-0.1
Methylpropyl ether	22.05	22.31	+1.2	22.36	+1.4
Methyl-n-butyl ether	27.02	26.93	-0.3	27.01	0
3-Chlorobenzaldehyde ^a	36.89	35.80	-2.9	35.65	-3.4
1-Methoxy-2-nitrobenzene ^a	36.89	38.16	+3.4	38.31	+3.8
1,3-Dichloro-2-butanone ^a	29.92	30.42	+1.7	29.18	-2.5
Diethylcamphoric acid ester	67.35	67.72	+0.5	67.86	+0.7
t-Butylphenylketone	50.27	49.41	-1.7	49.36	-1.8
N-Containing Compounds					
1-Aminobutane	24.08	24.09	0	24.02	-0.2
Triethylamine	33.79	33.85	+0.2	33.64	-0.4
Dimethylpentylamine	38.28	38.47	+0.5	38.30	0
Cyclopropylcyanide	19.09	20.69	+8.3	18.97	-0.6
Chlorotrinitromethane ^a	29.72	28.11	-5.4	28.57	-3.8
2,4-Dimethylquinoline	51.20	50.20	-1.9	51.58	+0.7
1-Methoxy-2-nitrobenzene ^a	36.89	38.16	+3.4	38.31	+3.8
Halide-Containing Compounds					
3-Chloropentane	30.16	30.16	0.0	30.09	+0.2
1-Bromobutane	28.35	28.44	+0.3	28.32	-0.1
1-Iodoheptane	42.89	42.71	-0.4	42.81	-0.1
3-Chlorobenzaldehyde ^a	36.89	35.80	-2.9	35.65	-3.4
1,3-Dichloro-2-butanone ^a	29.92	30.42	+1.7	29.18	-2.5
Chlorotrinitromethane ^a	29.72	28.11	-5.4	28.57	-3.8
3-Chloro-1,3-octadiene	43.83	43.08	-1.7	43.05	-1.7
Decachloro-1,5-hexadiene	76.73	77.64	-1.2	77.14	+0.5
Average Absolute Error (N = 29)			1.6	1.1	

a. Compounds listed twice because they fit two categories.

b. Source: Refs. 3 and 13.

TABLE 26-3

Observed Molar Refraction versus Values Estimated by
Hansch's Method

Compound	Observed ^a R_D (cm ³)	Estimated R_D (cm ³)	Error (%)
2-Methoxyethylbenzoic acid, ethyl ester	49.44	49.67	+0.5
2-Bromo-4-methylphenol	40.08	40.68	+1.5
4-Allylnaphthalene	57.33	57.32	0.0
1,6-Naphthylenediamine	53.77	53.67	-0.2
1,8-Naphthalenedicarboxylic acid, diethyl ester	77.31	77.76	+0.5
1-Naphthonitrile	50.31	49.16	-2.2
Nicotine	49.49	49.67	+0.4
3-Hydroxystyrene	38.94	38.17	-2.0
1-Naphthyl azide	53.00	53.03	0.0
1-Dichlorophosphino- 4-isopropylbenzene	60.66	60.73	+0.1
Average absolute error (N = 10)			0.7

a. Calculated by Eq. 26-2, using measured values of n and ρ from Ref. 16.

highly reliable because of the small sample set. However, the method does appear to be a very accurate means of estimating R_D for aromatic compounds; verification of this finding must await further testing.

The method errors given above are for the estimation of R_D , which must be combined with ρ and M in Eq. 26-3 to calculate n . A 1% error in R_D will typically translate into an error of $\sim 0.3\%$ in n , while a 5% error in R_D will typically translate into an error of $\sim 1\text{-}2\%$ in n . The method error for a particular estimated value of n should be calculated using the appropriate values of ρ and M . Details of methods for calculating propagated errors are given in Appendix C.

26-4 EISENLOHR'S METHOD

The method of Eisenlohr [1] allows calculation of R_D by simple addition of atomic and structural group contributions. The values of the increments are listed in Table 26-4. As stated earlier, estimates by this method are generally within $\pm 5\%$ of observed values. Gold and Ogle [2]

list the following average errors and 95% confidence limits of R_D for N number of compounds:

	Average Error (%)	95% Confidence Limit
All organics (N=177)	-0.26	$\pm 4.53 \text{ cm}^3$
Polar organics (N=99)	-0.34	$\pm 3.43 \text{ cm}^3$
Nonpolar organics (N=18)	+0.19	$\pm 10.55 \text{ cm}^3$

For the sample of 29 selected compounds listed in Table 26-2, the average absolute error in R_D is 1.3%.

TABLE 26-4

Atomic and Structural Contributions to Molar Refraction
by Additive Method of Eisenlohr

Group	Contribution (cm^3)	Group	Contribution (cm^3)
$-\text{CH}_2-$	4.618	O(hydroxyl)	1.525
C	2.418	O(ether)	1.643
H	1.100	O(carbonyl)	2.211 ^b
S as SH	7.69	OO(ester)	3.736 ^b
S as RSR	7.97	N(pri-amine)	2.322
S as RCNS	7.91	N(sec-amine)	2.502
S as RSSR	8.11	N(tert-amine)	2.840
F	0.95 ^a	N(nitrile)	5.516 ^c
Cl	5.967	Double bond	1.733
Br	8.865	Triple bond	2.398
I	13.900		

a. Only for one F attached to C. (1.1 for each F in polyfluorides.)

b. Includes allowance for double bond.

c. Includes allowance for triple bond.

Source: Adapted from Gold and Ogle [2].

Basic Steps

- (1) Calculate the molecular weight (M) of the compound and find the density (ρ) at the temperature of interest. (Methods for estimating density are detailed in Chapter 19.)

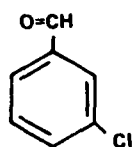
- (2) Draw the structure of the compound.
- (3) Total the incremental values from Table 26-4, accounting for all bonds and atoms. The sum is R_D , in cm^3 .
- (4) Using Eq. 26-3, determine n .

Example 26-1 Estimate n_D^{20} for *m*-chlorobenzaldehyde, $\text{C}_7\text{H}_5\text{OCl}$.

- (1) $M = 140.57 \text{ g/mol}$

$$\rho = 1.2410 \text{ g/cm}^3 \text{ at } 20^\circ\text{C} [16]$$

- (2) The structure is:



- (3) From Table 26-4,

7 C = 7 (2.418)	=	16.926
5 H = 5 (1.100)	=	5.500
1 Cl	=	5.967
1 carbonyl O	=	2.211
3 dbl bonds = 3 (1.733)	=	5.199
		$R_D = 35.803 \text{ cm}^3$

- (4) Substitute the values of R_D , ρ , and M into Eq. 26-3:

$$n = \sqrt{\frac{140.57 + 2(1.2410)(35.803)}{140.57 - (1.2410)(35.803)}} = 1.545$$

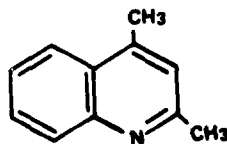
The observed value of n_D^{20} is 1.565 [13], indicating an error of -1.3%.

Example 26-2 Estimate n_D^{20} for 2,4-dimethylquinoline, $\text{C}_{11}\text{H}_{11}\text{N}$.

- (1) $M = 157.22 \text{ g/mol}$

$$\rho = 1.0611 \text{ g/cm}^3 \text{ at } 20^\circ\text{C} [16]$$

- (2) The structure is:



(3) From Table 26-4,

$$\begin{array}{rcl}
 11 \text{ C} = 11 (2.418) & = & 26.598 \\
 11 \text{ H} = 11 (1.100) & = & 12.100 \\
 1 \text{ } t\text{-amine N} & = & 2.840 \\
 5 \text{ dbl bonds} = 5 (1.733) & = & 8.665 \\
 \hline
 R_D & = & 50.203 \text{ cm}^3
 \end{array}$$

(4) Substitute the values of R_D , ρ , and M into Eq. 26-3:

$$n = \sqrt{\frac{157.22 + 2 (1.0611) (50.203)}{157.22 - (1.0611) (50.203)}} = 1.593$$

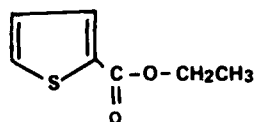
This underestimates the observed value, 1.6075 [13], by 0.9%.

Example 26-3 Estimate n_D^{20} for the ethyl ester of 2-thiophenecarboxylic acid, $\text{C}_7\text{H}_8\text{O}_2\text{S}$.

(1) $M = 156.22 \text{ g/mol}$

$$\rho = 1.1623 \text{ g/cm}^3 \text{ at } 16^\circ\text{C} [16]$$

(2) The structure is:



(3) From Table 26-4,

$$\begin{array}{rcl}
 7 \text{ C} = 7 (2.418) & = & 16.926 \\
 8 \text{ H} = 8 (1.100) & = & 8.800 \\
 1 \text{ OO (ester)} & = & 3.736 \\
 1 \text{ S as RSR} & = & 7.97 \\
 2 \text{ dbl bonds} = 2 (1.733) & = & 3.466 \\
 \hline
 R_D & = & 40.90 \text{ cm}^3
 \end{array}$$

(4) Substitute the values of R_D , ρ , and M into Eq. 26-3:

$$n = \sqrt{\frac{156.22 + 2 (1.1623) (40.90)}{156.22 - (1.1623) (40.90)}} = 1.520 \text{ (at } 16^\circ\text{C)}$$

The measured value of n cited in the literature is 1.5248 at 20°C [13]. Using the approximation that n decreases 5×10^{-4} per Celsius degree rise in temperature (§ 26-7), the estimated value of n adjusted to 20°C is $1.520 - (20 - 16) (5 \times 10^{-4}) = 1.518$. The error in the temperature-adjusted value is -0.45% .

26-5 VOGEL'S METHODS

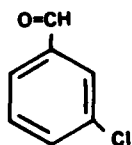
The methods of Vogel [13,14] allow the calculation of molar refractions for the C and F lines of hydrogen and G line of mercury as well as the sodium D line. Direct computation of n_D^{20} is also possible, whereas Eisenlohr's method requires its computation from R_D and the density of the compound. The incremental values for the group contribution method are listed in Table 26-5. Vogel's method based on bond increments [14] is not discussed here but is probably equally accurate. The accuracy of the group contribution method is not stated in the literature; for a sample group of the compounds tested in Table 26-5, however, the average absolute error (1.1%) was slightly less than that of Eisenlohr's procedure.

Basic Steps

- (1) Calculate the molecular weight (M) of the compound. For estimation of R_D or n_D at temperatures other than 20°C , find the density of the compound at the temperature of interest.
- (2) Draw the structure of the compound.
- (3) Total the incremental values of R_D or Mn_D^{20} from Table 26-5 for all bonds, atoms, and molecular groups. The sum is either $R_D(\text{cm}^3)$ or Mn_D^{20} .
- (4) To determine n_D^{20} , divide Mn_D^{20} by the molecular weight of the compound. If R_D was calculated, use Eq. 26-3 to obtain n_D^{20} .

Example 26-4 Estimate n_D^{20} for *m*-chlorobenzaldehyde, $\text{C}_7\text{H}_5\text{OCl}$

- (1) $M = 140.57 \text{ g/mol}$
- (2) The structure is:



- (3) The increments of Mn_D^{20} from Table 26-5 are:

1 C_6H_5	=	122.03
-1 H	=	+2.56
1 Cl	=	50.41
1 CO (carbonyl)	=	42.41
1 H	=	-2.56
<hr/>		
Mn_D^{20}		= 214.85 g/mol

TABLE 26-5

Atomic, Structural, and Group Increments for Vogel's Method

Group ^a	R _C	R _D	R _F	R _G	Mn _D ²⁰
CH ₂	4.624	4.647	4.695	4.735	20.59
H (in CH ₂)	1.026	1.028	1.043	1.040	-2.56
C (in CH ₂)	2.572	2.591	2.601	2.655	25.71
O (in ethers)	1.753	1.764	1.786	1.805	22.74
O (in acetals)	1.603	1.607	1.618	1.627	22.41
CO (in carbonyls)	4.579	4.601	4.654	4.702	42.41
CO (in methyl ketones)	4.730	4.758	4.814	4.874	42.42
COO (in esters)	6.173	6.200	6.261	6.315	64.14
OH (in alcohols)	2.536	2.546	2.570	2.588	23.94
CO ₂ H	7.191	7.226	7.308	7.368	63.98
Cl	5.821	5.844	5.918	5.973	50.41
Br	8.681	8.741	8.892	9.011	118.07
I	13.825	13.954	14.310	14.620	196.27
F	0.81	0.81	0.79	0.78	21.84
NH ₂ (in primary aliphatic amines)	4.414	4.438	4.507	4.570	22.64
NH (in secondary aliphatic amines)	3.572	3.610	3.667	3.732	23.34
NH (in secondary aromatic amines)	4.548	4.678	5.000	5.273	29.52
N (in tertiary aliphatic amines)	2.698	2.744	2.820	2.914	24.37
N (in tertiary aromatic amines)	4.085	4.243	4.675	5.155	30.23
NO (nitroso)	5.130	5.200	5.397	5.577	43.14
O•NO (nitrite)	7.187	7.237	7.377	7.507	62.27
NO ₂ (nitro)	6.662	6.713	6.823	6.918	65.61
N•NO (nitrosoamine)	7.748	7.850	8.100	8.358	69.67
S (in sulfides)	7.852	7.921	8.081	8.233	52.86
S ₂ (in disulfides)	15.914	16.054	16.410	16.702	106.52
SH (in thiols)	8.691	8.757	8.919	9.057	50.20
CS (in xanthates)	12.84	13.07	13.67	14.22	77.20
SCN (in thiocyanates)	13.313	13.400	13.603	13.808	88.90
NCS (in isothiocyanates)	15.445	15.615	15.980	16.300	93.11
Carbon-carbon double bond	1.545	1.575	1.672	1.720	-6.07
Carbon-carbon triple bond, terminal	1.959	1.977	2.061	2.084	-12.56
CN (in nitriles)	5.431	5.459	5.513	5.561	36.46
Three-carbon ring	0.592	0.614	0.656	0.646	-4.72
Four-carbon ring	0.303	0.317	0.332	0.322	-4.67
Five-carbon ring	-0.19	-0.19	-0.19	-0.22	-4.56
Six-carbon ring	-0.15	-0.15	-0.16	-0.17	-3.53
CO ₃ (carbonates)	7.662	7.696	7.754	7.818	86.35

(continued)

TABLE 26-5 (Continued)

Group ^a	R _C	R _D	R _F	R _G '	Mn _D ²⁰
SO ₃ (sulfites)	11.273	11.338	11.468	11.550	118.09
NO ₃ (nitrates)	8.973	9.030	9.170	9.293	87.59
SO ₄ (sulfates)	11.050	11.090	11.153	11.225	138.86
PO ₄ (orthophosphates)	10.733	10.769	10.821	10.905	139.74
CH ₃	5.636	5.653	5.719	5.746	18.13
C ₂ H ₅	10.260	10.300	10.414	10.481	38.72
C ₃ H ₇ ⁿ	14.895	14.965	15.125	15.235	59.25
C ₃ H ₇ ⁱ	14.905	14.975	15.145	15.255	58.95
C ₄ H ₉ ⁿ	19.500	19.585	19.800	19.950	79.81
C ₄ H ₉ ⁱ	19.530	19.620	19.840	19.990	79.54
C ₄ H ₉ ^s	19.330	19.420	19.625	19.775	80.21
C ₅ H ₁₁ ⁿ	24.140	24.250	24.515	24.700	100.46
C ₅ H ₁₁ ⁱ (from the synthetic alcohol)	24.095	24.195	24.460	24.650	100.30
C ₅ H ₁₁ ⁱ (from fermentation alcohol)	24.170	24.280	24.540	24.720	100.21
C ₆ H ₁₃ ⁿ	28.725	28.855	29.160	29.385	121.10
C ₇ H ₁₅ ⁿ	33.395	33.550	33.905	34.170	141.75
C ₈ H ₁₇ ⁿ	37.960	38.135	38.535	38.830	162.43
C ₃ H ₅ (allyl)	14.425	14.520	14.745	14.920	57.60
C ₆ H ₅ ^b	25.136	25.359	25.906	26.356	122.03

a. Superscripts: n = straight chain; i = iso-alkyl; s = sec-alkyl.

b. Benzene ring missing one hydrogen. This value is useful for calculating R_D and Mn_D for mono-substituted benzenes. No ring correction should be applied.

Source: Vogel [13].

(4) Divide Mn_D²⁰ by M:

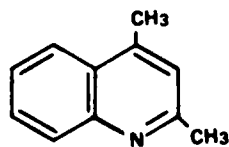
$$214.85/140.57 = 1.528$$

The literature value of n_D²⁰ is 1.565 [16], giving an error of -2.3%.

Example 26-5 Estimate n_D²⁰ for 2,4-dimethylquinoline, C₁₁H₁₁N.

(1) M = 157.22 g/mol

(2) The structure is:



(3) The increments of M_n^{20} from Table 26-5 are:

9 C	=	9 (25.71)	=	231.39
5 H	=	5 (-2.56)	=	-12.80
5 dbl bonds	=	5 (-6.07)	=	-30.35
2 CH ₃	=	2 (18.13)	=	36.26
1 N (tertiary aromatic amine)	=		=	30.23
2 6-membered rings ¹	=	2 (-3.53)	=	-7.06
				$M_n^{20} = 247.67 \text{ g/mol}$

(4) Divide this answer by M:

$$247.67/157.22 = 1.5753$$

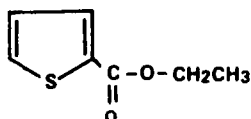
The value of n_D^{20} reported in the literature is 1.6075 [16]; the error is thus -2.0%.

Example 26-6 Estimate R_D for the ethyl ester of 2-thiophenecarboxylic acid, $C_7H_8O_2S$, at 16°C.

(1) $M = 156.22 \text{ g/mol}$

$$\rho = 1.1623 \text{ g/cm}^3 \text{ at } 16^\circ\text{C} [16]$$

(2) The structure is:



(3) The increments of R_D from Table 26-5 are:

1 5-membered ring ²	=	-0.19
1 S (sulfide)	=	7.921
1 COO	=	6.200
1 C ₂ H ₅	=	10.300
2 dbl bonds = 2 (1.575)	=	3.150
4 C	=	4 (2.591) = 10.364
3 H	=	3 (1.028) = 3.084
$R_D = 40.83 \text{ cm}^3$		

The value predicted from the Lorentz-Lorenz equation using $\rho = 1.1623$ at 16°C is 41.18 cm³, indicating a -0.8% error.

1. The table indicates 6-carbon rings; it is assumed this applies to 6-membered rings.
2. The table indicates a 5-carbon ring; it is assumed this value applies to 5-membered rings.

26-6 HANSCH'S METHOD

The method of Hansch *et al.* [4] is, like the previous recommended methods, a simple approach to the calculation of R_D using atomic and group fragment constants. The method is limited to substituted benzene compounds. The incremental values of R_D for approximately 240 aromatic substituents are given in Table 26-6. The arrangement of substituents in the table follows alphabetical order, beginning with the atom attached to the benzene ring. Within each group, C and H are listed first, with the remaining atoms sorted alphabetically. If there is no C, then H precedes the alphabetical arrangement, and if C and H are not in the substituent group, the group follows alphabetically.

The substituent R_D values in Table 26-6 may also be used for substituted benzene compounds with more than one substituent. However, interactions between ortho substituents may affect the R_D values in an unknown way; thus, methods errors for ortho-substituted benzenes may be larger than for those that contain only meta or para substituents. When the compound has more than one substituent, the R_D for C_6H_6 is diminished by 1.03 (the value of one H atom) for every substituent after the first.


The method error has not been established. For mono-substituted benzenes, one would expect very high accuracy, since the substituent R_D values were presumably derived from measured values of n and ρ for that particular compound. For compounds with two or more substituents, the error is likely to vary with the nature of the substituents and their relative positions on the ring. For the small sample set in Table 26-3, the error ranged from 0 to 2.2% and averaged 0.7%.

Basic Steps

- (1) Calculate the molecular weight (M) of the compound, and find the density (ρ) at the temperature of interest. (Methods for estimating density are provided in Chap. 19.)
- (2) Draw the molecular structure.
- (3) For mono-substituted benzenes, find R_D for the substituent in Table 26-6 and add it to the R_D for C_6H_6 (25.36). If the compound has two or more substituents on the benzene ring, subtract 1.03 (the value for one H atom) from the total for every substituent *after* the first.
- (4) Calculate n_D with Eq. 26-3.

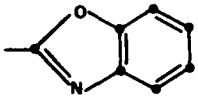
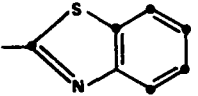
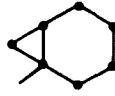
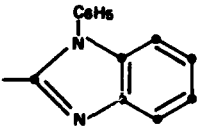
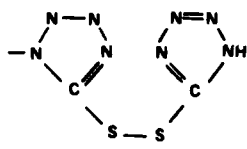
TABLE 26-6

Hansch's Group Contributions to R_D of Aromatic Compounds

Group	Contribution	Group	Contribution
B(OH) ₂	11.04	CH=CHCN	16.23
Br	8.88	C≡CCH ₃	14.14
CBr ₃	28.81	CH=CHCHO	16.88
CCl ₃	20.12	CH=CHCOOH	17.91
CF ₃	5.02	CH ₂ CH=CH ₂	14.49
CN	6.33	Cyclopropyl	13.53
COO ⁻	6.05	CH ₂ COCH ₃	15.06
CHO	6.88	CO ₂ C ₂ H ₅	17.47
COOH	6.93	CH ₂ OC=O(CH ₃)	16.48
CH ₂ Br	13.39	CH ₂ CH ₂ CO ₂ H	16.52
CH ₂ Cl	10.49	3,4-(CH ₂ CH ₂ CH ₂)	13.94
CH ₂ I	18.60	C ₃ H ₇	14.96
CONH ₂	9.81	CH(CH ₃) ₂	14.98
CH=NOH	10.28	CH ₂ N(CH ₃) ₂	18.74
C=O(NHOH)	11.22	CF ₂ CF ₂ CF ₂ CF ₃	17.65
CH ₃	5.65	2-Thienyl	24.04
CH ₂ OH	7.19	3,4-(CH=CHCH=CH)	17.47
CH ₂ NH ₂	9.09	CH=CHCOCH ₃	21.10
C=O(CF ₃)	11.17	Cyclobutyl	17.88
3,4-(CF ₂ OCF ₂)	10.19	3,4-(CH ₂) ₄	18.59
C≡CH	9.55	C ₄ H ₉	19.59
CH ₂ SCF ₃	17.59	C(CH ₃) ₃	19.62
CH ₂ SO ₂ CF ₃	17.51	CH ₂ Si(CH ₃) ₃	29.61
CH ₂ CN	10.11	4-Pyridyl	23.03
CH=CHNO ₂ (trans)	16.42	CH=CHCO ₂ C ₂ H ₅	27.21
CH=CH ₂	10.99	Cyclopentyl	22.02
COCH ₃	11.18	C ₅ H ₁₁	24.25
CO ₂ CH ₃	12.87	(CH ₂) ₃ N(CH ₃) ₂	28.04
CH ₂ COOH	11.88	C ₆ Cl ₅	49.53
C=O(NHCH ₃)	14.57	C ₆ F ₅	23.98
CH ₂ CONH ₂	14.41	C ₆ H ₂ [2,4,6-(NO ₂) ₃]	42.21
C=S(NHCH ₃)	22.33	C ₆ H ₅	25.36
C ₂ H ₅	10.30		24.80
C≡CCF ₃	14.13	Cyclohexyl	29.69
CF(CF ₃) ₂	13.44		
C(OH)(CF ₃) ₂	15.18		
CH=CHCF ₃ (trans)	15.57		
CH=CHCF ₃ (cis)	15.57		

(continued)

TABLE 26-6 (Continued)

Group	Contribution	Group	Contribution
	32.74	I	13.94
2-Benzoxazolyl		IO	39.06
	38.88	IO ₂	63.51
2-Benzthiazolyl		NO	5.2
C=O(C ₆ H ₅)	30.33	NO ₂	7.36
CH=NC ₆ H ₅	33.01	NNN	10.2
CH ₂ C ₆ H ₅	30.01	NH ₂	5.42
CH(OH)C ₆ H ₅	31.52	NHOH	7.22
	29.44	NHNH ₂	8.44
C≡CC ₆ H ₅	33.21	NHSO ₂ NHSO ₂ -NH ₂	28.40
CH=CHC ₆ H ₅	34.17	5-Cl-1-tetrazolyl	23.16
CH ₂ CH ₂ C ₆ H ₅	34.65	N=CCl ₂	18.35
CH=CHCOC ₆ H ₄ -(4-NO ₂)	45.68	N=C=O	8.82
CH=CHCOC ₆ H ₅	40.25	N=C=S	17.24
Ferrocenyl	48.24	5-Azido-1-tetrazolyl	26.85
Adamantyl	40.63	NHCN	10.14
	59.08	1-Tetrazolyl	18.33
1-Phenyl-2-benzimidazolyl		5-OH-1-tetrazolyl	19.77
CO ₂ CH(C ₆ H ₅) ₂	60.37	5-SH-1-tetrazolyl	26.06
Cl	6.03	NHCHO	10.31
F	0.92	NHCONH ₂	13.72
GeBr ₃	36.35	NHCSNH ₂	22.19
GeCl ₃	25.85	NHCH ₃	10.33
GeF ₃	6.95	NHSO ₂ CH ₃	18.17
H	1.03	N(CF ₃) ₂	14.28
HgCH ₃	19.43	NHCOCF ₃	14.30
			49.17
		NHCOCH ₂ Cl	19.77
		NHCOCH ₃	14.93
		NHCSCH ₃	23.40
		NHC ₂ H ₅	14.98
		N(CH ₃) ₂	15.55
		N(SO ₂ CH ₃) ₂	31.22
		N=NN(CH ₃) ₂	20.88
		NHCOC ₂ H ₅	19.58
		NHCO ₂ C ₂ H ₅	21.18

(continued)

TABLE 26-6 (continued)

Group	Contribution	Group	Contribution
NHCONHC ₂ H ₅	23.19	PH ₂	12.19
NHCSNHC ₂ H ₅	31.66	P(Cl)N(CH ₃) ₂	27.01
NHCOCH(CH ₃) ₂	24.25	PO(CH ₃) ₂	19.93
NHCH ₂ CO ₂ C ₂ H ₅	25.82	PO(OCH ₃) ₂	21.87
NHC ₄ H ₉	24.26	P(CH ₃) ₂	21.19
N=NC ₆ H ₅	31.31	P(OC ₂ H ₅) ₂	32.42
NHC ₆ H ₅	30.04	PO(OC ₂ H ₅) ₂	31.16
NHSO ₂ C ₆ H ₅	37.88	PO(Cl)C ₆ H ₄ -3-F	39.49
N=CHC ₆ H ₅	33.01	P(Cl)C ₆ H ₄ -3-F	40.75
NHCOC ₆ H ₅	34.64	PS(Cl)C ₆ H ₄ -3-F	47.62
N=NC ₆ H ₃ -(2-OH)(5-CH ₃)	37.45	P(Cl)C ₆ H ₅	40.99
N=CHC ₆ H ₄ -(4-OCH ₃)	39.29	P(H)C ₆ H ₄ -3-F	36.14
NHCOC ₆ H ₄ -(4-OCH ₃)	41.03	PO(OC ₃ H ₇) ₂	40.46
N(C ₆ H ₅) ₂	54.96	P(OCH ₃)C ₆ H ₄ -3-F	41.68
OH	2.85	PO(CH ₃)C ₆ H ₄ -3-F	39.37
3,4-(OCF ₂ O)	8.95	P(CH ₃)C ₆ H ₄ -3-F	40.63
OCF ₃	7.86	PO(C ₄ H ₉) ₂	47.81
OCHF ₂	7.86	PO(C ₆ H ₅) ₂	59.29
OCONH ₂	11.28	P(C ₆ H ₅) ₂	60.55
3,4-(OCH ₂ O)	8.96	PS(C ₆ H ₅) ₂	67.42
OCH ₃	7.87	SO ₂ (F)	8.65
OSO ₂ CH ₃	16.99	SF ₅	9.89
OCF ₂ CHFCI	17.30	SH	9.22
OCOCH ₃	12.47	SO ₂ (NH ₂)	12.28
OCH ₂ COOH	13.99	SCCl ₃	28.34
OEt	12.47	S=O(CF ₃)	13.07
OPO(OCH ₃) ₂	22.02	SO ₂ (CF ₃)	12.86
OCH(CH ₃) ₂	17.06	SCF ₃	13.81
OC ₃ H ₇	17.06	SCN	13.40
OC ₄ H ₉	21.66	SCHF ₂	13.81
OC ₅ H ₁₁	26.26	SOCHF ₂	13.28
OC ₆ H ₅	27.68	SO ₂ CHF ₂	13.08
OSO ₂ C ₆ H ₅	36.70	SOCH ₃	13.70
O-β-glucose	36.53	SO ₂ CH ₃	13.49
OCOC ₆ H ₅	32.33	SCH ₃	13.82
POCl ₂	20.16	SCF ₂ CHF ₂	18.40
PCl ₂	21.42	SCOCH ₃	18.42
POF ₂	9.58	SC ₂ H ₅	18.42
PF ₂	11.02	SO ₂ (C ₆ H ₅)	33.20
PSCl ₂	28.29	SC ₆ H ₅	34.29

(continued)

TABLE 26-6 (Continued)

Group	Contribution	Group	Contribution
SeCF ₃	16.32	SiF ₃	7.62
SeCN	16.82	Si(CH ₃) ₃	24.96
SeCH ₃	17.03	Si(CH ₃) ₂ [OSi-(CH ₃) ₃]	43.64
SiBr ₃	32.76	Si(CH ₃)[OSi-(CH ₃) ₃] ₂	62.32
SiCl ₃	23.85	Si[OSi(CH ₃) ₃] ₃	80.99

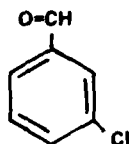
Source: Hansch *et al.* [4].

Example 26-7 Estimate n_D^{20} for *m*-chlorobenzaldehyde.

(1) $M = 140.57 \text{ g/mol}$

$\rho = 1.2410 \text{ g/cm}^3 \text{ (20}^\circ\text{C)}$

(2) The structure of the molecule is:



(3) Total the incremental values in Table 26-6:

$$\text{C}_6\text{H}_5 = 25.36$$

$$\text{Cl} = 6.03$$

$$\text{CHO} = 6.88$$

$$-\text{H} = -1.03$$

$$R_D = 37.24 \text{ cm}^3$$

(4) Substitute the above in Eq. 26-3:

$$n_D^{20} = \sqrt{\frac{140.57 + 2(1.2410)(37.24)}{140.57 - (1.2410)(37.24)}} = 1.571$$

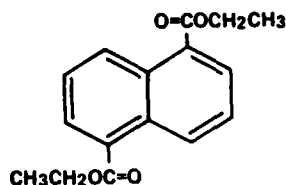
The observed value is 1.565 [13], indicating an error of +0.4%.

Example 26-8 Estimate n_D^{20} for 1,8-naphthalene-dicarboxylic acid, diethyl ester.

(1) $M = 273.3 \text{ g/mol}$

$\rho = 1.1399 \text{ g/cm}^3 \text{ (at 70}^\circ\text{C)}$

- (2) The structure of the molecule is



- (3) Total the incremental values from Table 26-6:

$$\begin{aligned}
 \text{C}_6\text{H}_5 &= 25.36 \\
 3,4(\text{CH}=\text{CH}-\text{CH}=\text{CH}) &= 17.47 \\
 2 \text{ CO}_2\text{C}_2\text{H}_5 &= 2(17.47) = 34.94 \\
 -3\text{H} &= -3(1.03) = -3.09 \\
 R_D &= 74.68 \text{ cm}^3
 \end{aligned}$$

- (4) Substitute the above in Eq. 26-3:

$$n_D^{70} = \sqrt{\frac{273.3 + 2(1.1399)(74.68)}{273.3 - (1.1399)(74.68)}} = 1.535$$

The literature value is 1.559 [13], indicating an error of 1.5%.

26-7 EFFECTS OF TEMPERATURE ON n

The Lorentz-Lorenz equation (Eq. 26-2) reflects the theoretical relationship of R_D to n and ρ (which is temperature-dependent). Table 26-7 includes three other equations of empirical derivation which provide more accurate means to calculate n from R_D over a wide temperature range [7]. Of the listed equations, that by Eykman appears to be the most accurate. This equation has not received the exposure of the Lorentz-Lorenz equation, which appears (see Table 26-7) to give a positive bias in the error. Generally, the refractive index (n) decreases about 4×10^{-4} to 6×10^{-4} for each Celsius degree increase in temperature [12].

26-8 AVAILABLE DATA

Ward and Kurtz [15] list refractive indices for a large number of compounds, arranged by chemical class. References [6] and [8] also tabulate some values. Standard references such as [13] include values of n_D^{20} . Additional sources are listed in Appendix A.

26-9 SYMBOLS USED

- c = speed of light in a vacuum = 3×10^{10} cm/s in Eq. 26-1
 M = molecular weight (g/mol)

TABLE 26-7

Methods of Deriving n from R_D

Method of	Formula ^a	$\left(\frac{\text{Deviation per } ^\circ\text{C of Temperature Change}^b}{\text{Temperature Change}^b} \right) \times 10^6$	
		Liquid Hydrocarbons (N = 14)	Liquid Non-Hydrocarbons (N = 34) ^c
Eykman	$\frac{n^2 - 1}{n + 0.4} = R_D \rho$	± 15	± 11
Lorentz-Lorenz	$\frac{n^2 - 1}{n^2 + 2} = R_D \rho$	$+47^d$	$+60^d$
Gladstone-Dale	$n - 1 = R_D \rho$	$+28$	-16
Ward-Kurtz	$\Delta n = 0.6 \Delta \rho$	± 24	± 56

a. The dependence of n on temperature is expressed here by equations containing density (ρ), which is a function of temperature.

b. Range of temperature change $\cong 16\text{-}79^\circ\text{C}$.

c. Average of 34 liquid non-hydrocarbons, including alcohols, saturated acids and esters, unsaturated acids, derivatives of phenols, aromatic esters, and aromatic ketones.

d. Deviation indicates positive bias for both chemical classes.

Source: Kurtz, Amon, and Sankin [7].

- N = number of compounds in sample
 n = refractive index (unitless)
 n_D = refractive index measured using light from sodium D line
 R_D = molar refraction (cm^3)
 T = temperature ($^\circ\text{C}$)
 v = velocity of light in medium in Eq. 26-1 (cm/s)

Greek

- λ = wavelength (nm)
 ρ = density (g/cm^3)
 χ = connectivity parameter

26-10 REFERENCES

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A

BIBLIOGRAPHY OF STANDARD CHEMICAL PROPERTY DATA SOURCES

This Appendix provides a listing of selected reference books which contain compilations of standard physical and chemical properties of organic compounds. It is meant to serve as a quick reference to important handbooks for standard parameters; it excludes environmental parameters such as the bioconcentration factor, process rate constants, and the octanol/water partition coefficient, which are adequately covered in the chapters covering these properties (see sections on "Available Data"). The listing is only for works covering organic compounds (although some may contain data on inorganics as well), and should be considered as supplemental to the listings given in the "Available Data" sections of each individual chapter.

Table A-1 indicates a number of published sources which may be consulted for data on the properties of interest to the users of this handbook. The numbers at the top of each column refer to the reference numbers in the bibliography. Although the properties listed do not distinguish between the gaseous and liquid state, most of the handbooks contain data for both phases or contain an identifier in the title of the reference. The user should be aware that some of the data in these sources have not been critically reviewed and that the referenced sources may contain scanty information or be specific to certain classes of chemicals. However, in all cases, we have cited the most recent edition of the publication so that the most up-to-date data will be available to the user.

TABLE A-1
 Compilations of Data for Common Properties of Organic Chemicals

Property	Source (Ref. No.)																				Other Ref.
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
Solubility in Water	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	21
Acid/Base Dissociation	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	21
Boiling Point	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	22
Heat of Vaporization	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	23
Vapor Pressure	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	24
Diffusion Coefficient	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	
Flash Point	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	22, 25
Density	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	
Surface Tension	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	
Interfacial Tension	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	
Viscosity	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	22
Heat Capacity	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	21, 25, 26
Thermal Conductivity	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	26
Dipole Moment	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	
Refractive Index	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	22
Melting Point	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	
Heat of Fusion	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	26
Critical Properties	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	25-28
Temperature	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	
Pressure	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	
Volume	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	
Critical Compressibility	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	

A wealth of information on chemical data is accessible through the National Bureau of Standards (NBS), Office of Standard Reference Data in Washington, D.C. This office administers a program of data compilations called the National Standard Reference Data System (NSRDS), which provides data in the areas of energy, environment, industry, materials and physical sciences. The industrial process data include information on thermodynamic, transport, and physical properties of industrially important chemicals. The physical science data include basic data and fundamental physical constants.

The data evaluated by the NSRDS program are brought to public attention in the following publications and journals:

- Journal of Physical and Chemical Reference Data — a quarterly review published for the NBS by the American Chemical Society and the American Institute of Physics.
- NSRDS-NBS Series — distributed through the Government Printing Office.
- Miscellaneous sources, such as technical society publications and on-line computer retrieval systems.

The NSRDS collects its data from a number of data centers which specialize in specific areas of chemical research. The addresses of data centers pertinent to this handbook are:

- Chemical Kinetics Information Center
Center for Thermodynamics and Molecular Science
Chemistry Building
NBS, Washington, D.C. 20234
Telephone: 301-921-2565
- Chemical Thermodynamics Data Center
Center for Thermodynamics and Molecular Science
Chemistry Building
NBS, Washington, D.C. 20234
Telephone: 301-921-2773
- Fundamental Constants Data Center
Center for Absolute Physical Quantities
Metrology Building
NBS, Washington, D.C. 20234
Telephone: 301-921-2701

- Thermodynamics Research Center
Texas A&M University
Department of Chemistry
College Station, Texas 77843
Telephone: 717-846-8765
or 717-845-4971

The types of reports available through the NBS often encompass a small class of chemicals, or at times, just one chemical. NSRDS data compilations have been indexed by property for the years 1964-1972 (Report No. NSRDS-NBS-55). The Journal of Physical and Chemical Reference Data updates its index once a year. The properties indexed include a broad spectrum of parameters including activity coefficient, diffusion coefficient, dipole moment, rate constants and surface tension.

An important publication of the Thermodynamics Research Center (one of the NSRDS data centers) is their *Selected Values of Properties of Hydrocarbons and Related Compounds* [29]. Category A of this publication (8 volumes) contained, as of September 1979, tables of physical and thermodynamic properties of hydrocarbons on 3,194 data sheets. Supplements of new and revised loose-leaf data sheets are issued irregularly to keep the work current.

Another publication series that may be of interest is available from Engineering Sciences Data Units, Ltd. (ESDU). A sampling of reports issued in 1979 included:

- 1) Viscosity of Liquid Aliphatic Hydrocarbons: Alkanes
- 2) Thermal Conductivity of Liquid Carboxylic Acids
- 3) Heat Capacity and Enthalpy of Liquids: Aliphatic Alcohols
- 4) Vapor Pressures and Critical Points of Liquids. XIV:
Aliphatic Oxygen-Nitrogen Compounds

Details on the availability of these and other reports in their Physical Data/Chemical Engineering series may be obtained from ESDU, 251-259 Regent Street, London W1R 7AD, England.

A very useful compilation of data sources for both inorganic and organic substances has been prepared by Armstrong and Goldberg [30] for the National Bureau of Standards.

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B

SIMPLE LINEAR REGRESSION

Cathy Campbell

B-1 INTRODUCTION

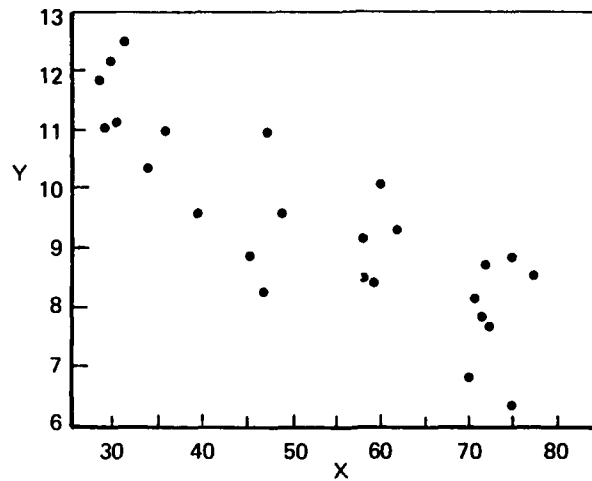
Many research projects involve the measurement of an independent, predictor or control variable (X) and a response or dependent variable (Y) for different values of X. The values of Y that are observed vary because of (a) the value of the control variable and (b) random error. When a researcher believes that the variation is basically linear, this can be expressed by assuming that the data follow a simple linear model:

$$Y = A + BX + \text{error} \quad (\text{B-1})$$

The errors in the model may be positive or negative but on the average will be equal to 0. Figure B-1 shows a plot of 25 (X, Y) observations that appear to follow the simple linear model. The original data are in Table B-1.

The quantities A, B, and $\sigma_{Y \cdot X}$ are the parameters (unknown constants) that describe the linear relationship and are defined as follows:

- A = intercept of regression line
- B = slope of regression line
- $\sigma_{Y \cdot X}$ = standard deviation of the errors, also called standard error of the estimate



Source: Adapted from Draper and Smith [1], P.9

FIGURE B-1 Scatter Plot of Twenty-five Observations of Two Variables

TABLE B-1

Twenty-five Observations of Two Variables

Observation Number	X	Y	Observation Number	X	Y
1	35.3	10.98	14	39.1	9.57
2	29.7	11.13	15	46.8	10.94
3	30.8	12.51	16	48.5	9.58
4	58.8	8.40	17	59.3	10.09
5	61.4	9.27	18	70.0	8.11
6	71.3	8.73	19	70.0	6.83
7	74.4	6.36	20	74.5	8.88
8	76.7	8.50	21	72.1	7.68
9	70.7	7.82	22	58.1	8.47
10	57.5	9.14	23	44.6	8.86
11	46.4	8.24	24	33.4	10.36
12	28.9	12.19	25	28.6	11.08
13	28.1	11.88			

Source: Draper and Smith [1], p. 8.

Linear regression analysis is the area of statistics which encompasses methods for:

- estimating the parameters of the simple linear model;
- determining if there is a "significant" linear relationship between X and Y;
- predicting future values of Y, given values of the control variable X.

The procedures used in a simple linear regression analysis are described in the following sections of this appendix:

- B-2 Examining the Data
- B-3 Parameter Estimation
- B-4 Evaluating the Regression
- B-5 Predicting Future Observations
- B-6 Symbols Used

The necessary data for performing a regression analysis consist of n pairs of observations, $\{(X_i, Y_i): i = 1, \dots, n\}$ which are usually arranged as in Table B-1. These data will be used throughout for demonstration purposes. The measurements were taken periodically on a steam plant, where

- X = average atmospheric temperature ($^{\circ}$ F) for a month
- Y = steam consumption (lb/mo)

B-2 EXAMINING THE DATA

Observed data for a linear regression problem represent a sample of an entire population of values that might have been observed. For the methods of linear regression to be valid, certain assumptions about the underlying population must be satisfied:

1. X and Y are linearly (not curvilinearly) related;
2. The long-run average of the errors is 0;
3. The errors are statistically independent; i.e., knowing the error for one observation gives no information about the sign or magnitude of the error for any other observation;
4. The errors are approximately symmetric around 0 and do not deviate dramatically from a normal distribution;

5. The average magnitude of the errors is constant for all values of X, called homoscedastic errors.

Before conducting a regression analysis, the analyst should examine the data to determine if these assumptions are (approximately) satisfied. For a given sample of data, none will be satisfied exactly, because the assumptions apply to the population that generates the data. Unless the observed data depart dramatically from these assumptions, simple linear regression is an appropriate analysis. Alternative analysis methods should be used if any of the assumptions appear to be severely violated.

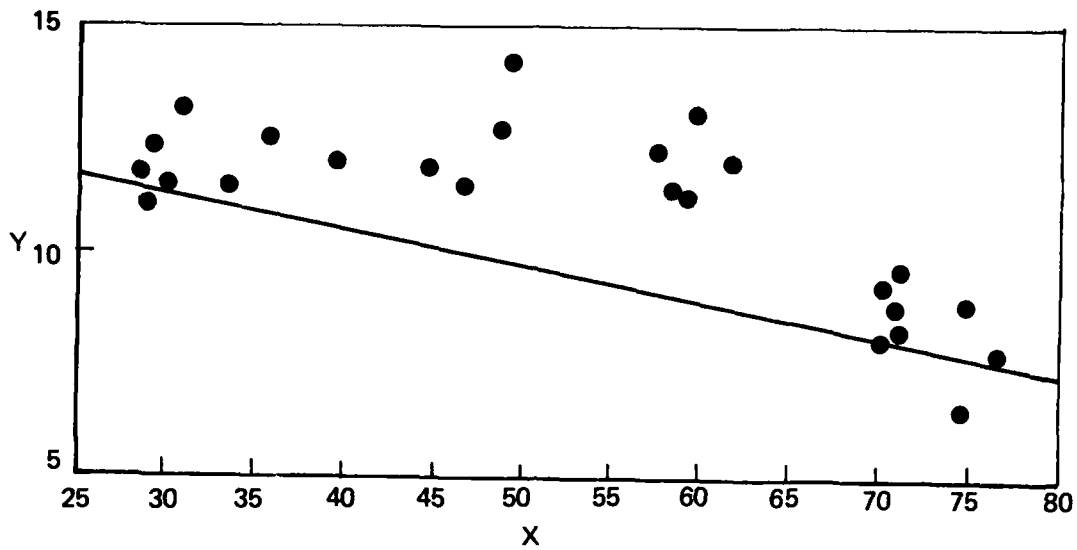
Making a scatterplot, as in Figure B-1, is the best way to examine the data when only two variables are observed and should be a routine first step of any regression analysis. Since the plot in Figure B-1 does not show anything unusual, linear regression analysis would be appropriate for these data.

Figure B-2 contains scatterplots that illustrate violation of assumptions (1), (3) (4), and (5). Violation of assumption (2) cannot be detected from a sample.

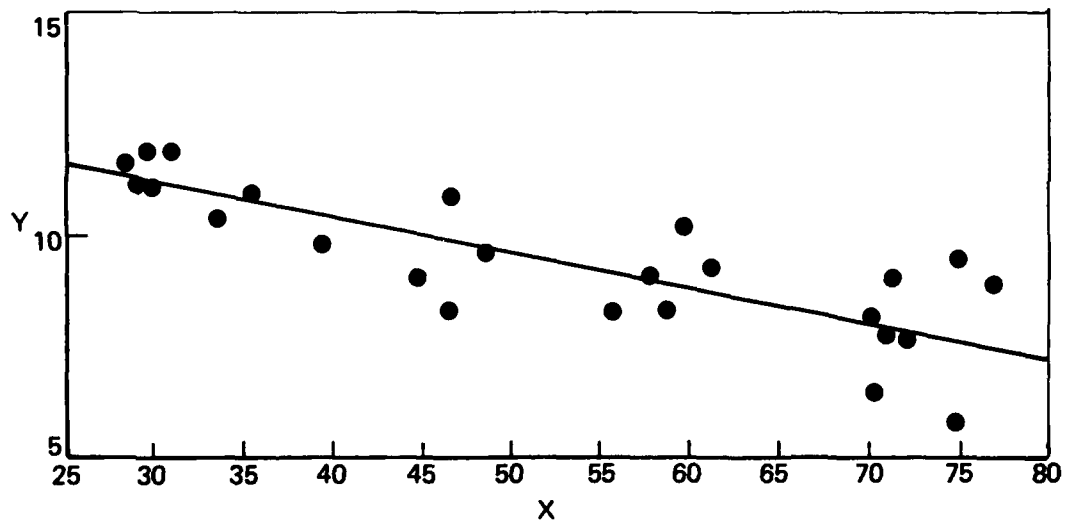
Assumption (3), independence of errors, may be in doubt when the observations are taken sequentially or when different people or instruments are used for separate parts of the data collection. (See Section B-4.)

Assumption (4) often fails because of the presence of outliers — observations which depart from the general pattern of the data; they show up very clearly in the scatterplot. Outliers are troublesome in regression analysis, because one or two unusual observations can unduly influence the results of an analysis. When outliers appear in the scatterplot, the following steps should be taken:

- (1) First determine if a simple recording error was made. Make the necessary correction, or delete the observation if correction is impossible.
- (2) If no error occurred, see if the observation was made under unusual but observable circumstances that would explain the strange value. If a valid cause can be found, delete the observation from the analysis.
- (3) When no cause for the outlier(s) can be found, perform two analyses — one that includes the observation(s) and one

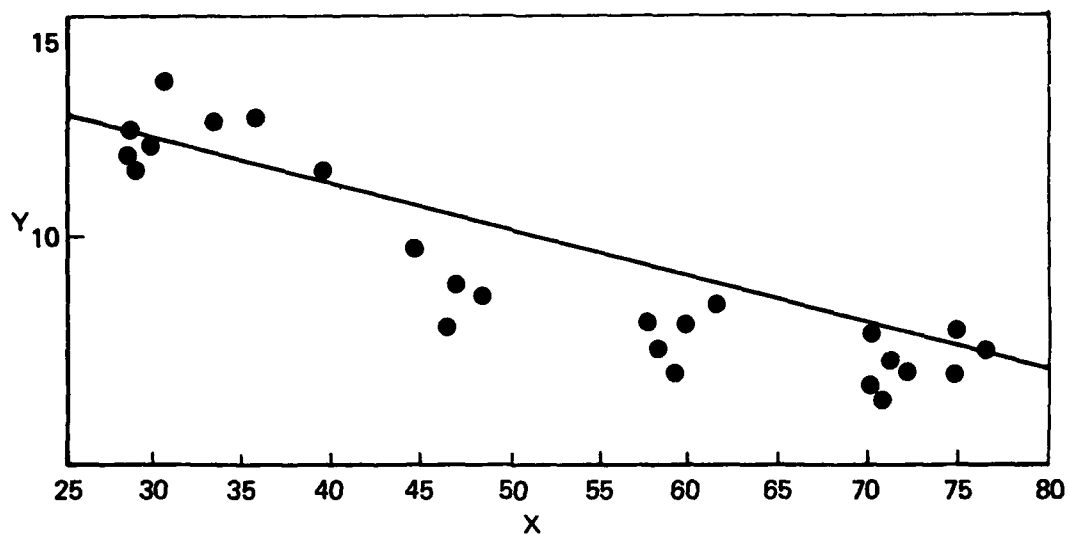


a. Plot Is Nonlinear

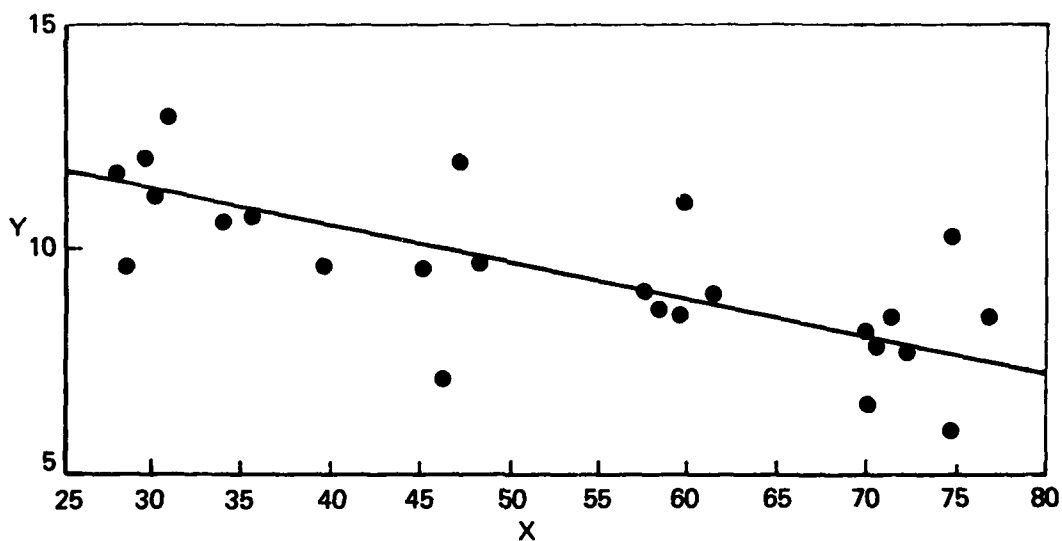


b. Variance Increases with X

FIGURE B-2 Violation of Regression Assumptions



c. Errors Are Correlated



d. Errors Are Not Normally Distributed

FIGURE B-2 Violation of Regression Assumptions (continued)

that excludes them. If the two analyses essentially agree, report the full analysis. If they disagree, report both and explain why they differ.

After making the scatterplot and determining that simple linear regression is appropriate, one can begin formal analysis of the data.

B-3 PARAMETER ESTIMATION

With limited data, one cannot determine exactly the parameters (A, B and $\sigma_{Y.X}$) of the regression equation (Eq. B-1). One must be satisfied with point estimates (single best values) and estimated standard errors that tell how far away from the "true" value the point estimate may be. Because of this uncertainty about the "true" values, it is recommended that parameter estimates be presented in the form of confidence intervals that realistically reflect the researcher's knowledge about the parameter value.

A confidence interval for a parameter B consists of two numbers, B_{lower} and B_{upper} (B_L and B_U), calculated from the sample data so that the researcher can say, "I am 95% (or 90%, 99%, etc.) confident that the true value of B lies between B_L and B_U ." If the statement is made with a high degree, say 99%, of confidence, the interval will be larger than if a low degree of confidence, say 70%, is chosen.

The principle of least squares is used in calculating the point estimates of A and B. Estimating A and B is equivalent to finding the slope and intercept of the best-fitting line through the sample data. The equation of the sample regression line is:

$$\hat{Y} = a + bX \quad (\text{B-2})$$

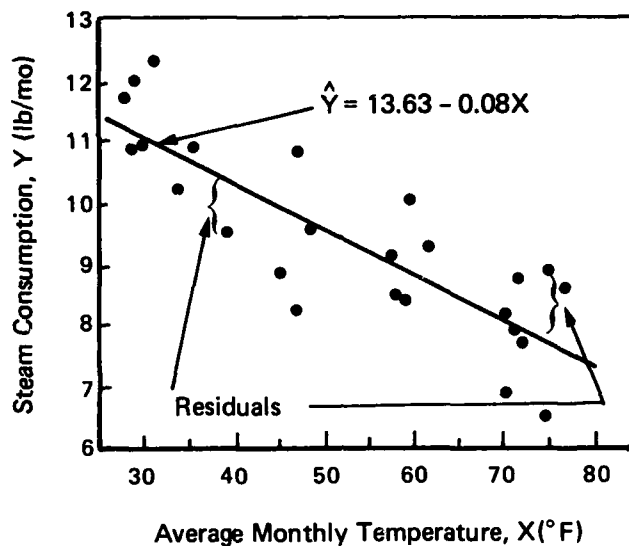
where

- a = estimate of A
- b = estimate of B
- \hat{Y} = predicted value of Y for a given X.

Estimates a and b are chosen so that the sum of the squared distances of the observed Y's from the Y's predicted by the sample regression line is as small as possible, i.e., so that

$$\sum_{i=1}^n (Y_i - a - bX_i)^2$$

is minimized. The quantity $Y_i - \hat{Y}_i = Y_i - a - bX_i$ is called the residual for the i th observation. See Figure B-3 for a display of these quantities. (The derivation of the regression equation is explained later in this section.)



Source: Adapted from Draper and Smith [1], p. 9

FIGURE B-3 Least-squares Regression Line

The least-squares estimate of B is:

$$b = \frac{\sum_{i=1}^n X_i Y_i - n \bar{X} \bar{Y}}{\sum_{i=1}^n X_i^2 - n \bar{X}^2} \quad (\text{B-3})$$

where

$$\bar{X} = \frac{1}{n} \sum_{i=1}^n X_i \text{ and } \bar{Y} = \frac{1}{n} \sum_{i=1}^n Y_i \quad (\text{B-4, -5})$$

are the sample means of X and Y. The estimate of A is

$$a = \bar{Y} - b\bar{X}. \quad (\text{B-6})$$

The estimate of $\sigma_{Y \cdot X}$ is

$$s_{Y \cdot X} = \sqrt{\frac{n-1}{n-2} (s_Y^2 - b^2 s_X^2)} \quad (\text{B-7})$$

where s_X^2 and s_Y^2 are the sample variances of X and Y:

$$s_X^2 = \frac{1}{n-1} \left(\sum_{i=1}^n X_i^2 - n \bar{X}^2 \right) \quad (\text{B-8})$$

$$s_Y^2 = \frac{1}{n-1} \left(\sum_{i=1}^n Y_i^2 - n \bar{Y}^2 \right) \quad (\text{B-9})$$

The sample standard deviation $s_{Y \cdot X}$ depends on the magnitude of the sum of squared residuals; it can also be expressed as

$$s_{Y \cdot X} = \sqrt{\frac{1}{n-2} \sum_{i=1}^n (Y_i - \hat{Y}_i)^2} \quad (\text{B-10})$$

but this is not a useful computing form.

To find confidence intervals for A and B, estimates of the standard errors (s.e.) of a and b must be calculated as follows:

$$\text{s.e. (a)} = s_{Y \cdot X} \sqrt{\frac{1}{n} + \frac{\bar{X}^2}{(n-1) s_X^2}} \quad (\text{B-11})$$

$$\text{s.e. (b)} = \frac{\sqrt{s_{Y \cdot X}^2}}{\sqrt{(n-1) s_X^2}} \quad (\text{B-12})$$

The magnitude of the estimated standard errors determines the width of the confidence intervals.

The actual form of (B_L, B_U) and (A_L, A_U) is given by

$$B_L = b - t_{1-\alpha/2} (n-2) \text{ s.e. (b)} \quad (\text{B-13})$$

$$B_U = b + t_{1-\alpha/2} (n-2) \text{ s.e. (b)}$$

and

$$A_L = a - t_{1-\alpha/2} (n-2) \text{ s.e. (a)} \quad (\text{B-14})$$

$$A_U = a + t_{1-\alpha/2} (n-2) \text{ s.e. (a)}$$

where $100(1 - \alpha) \%$ is the desired confidence level and $t_{1-\alpha/2}(n - 2)$ is the $100(1 - \alpha/2)$ percentile point of Student's t-distribution with $n-2$ degrees of freedom. The value of t can be read from tables found in any introductory statistics text; for convenience, a t -table is reproduced here as Table B-2.

Example B-1 In this sample, all of the preceding calculations are demonstrated and interpreted for the data in Table B-1.

- (1) The sample size, n , is 25. The mean (Eq. B-4) and standard deviation (Eq. B-8) of X are

$$\bar{X} = \frac{1}{n} \sum_{i=1}^n X_i = \frac{1315}{25} = 52.60$$

$$s_X = \sqrt{\frac{1}{n-1} \sum_{i=1}^n X_i^2 - n\bar{X}^2} = \sqrt{\frac{1}{24} [76323 - 25(52.60^2)]}$$

$$= 17.27$$

- (2) Performing the same calculations for Y gives

$$\bar{Y} = 9.424$$

$$s_Y = 1.63$$

- (3) The first step in calculating b is to multiply the X and Y values for each observation and total the products.

$$\sum_{i=1}^n X_i Y_i = 11821$$

- (4) Substituting in Eq. B-3,

$$b = \frac{\sum_{i=1}^n X_i Y_i - n\bar{X}\bar{Y}}{\sum_{i=1}^n X_i^2 - n\bar{X}^2} = \frac{11821 - (25)(52.60)(9.424)}{76323 - (25)(52.60^2)}$$

$$= -0.080$$

- (5) Since $a = \bar{Y} - b\bar{X}$ (Eq. B-6),
- $$a = 9.424 - (-0.080)(52.60)$$
- $$= 13.63$$

TABLE B-2

Upper Percentage Points of the t Distribution

Degrees of Freedom	1- α						
	0.75	0.90	0.95	0.975	0.99	0.995	0.9995
1	1.000	3.078	6.314	12.706	31.821	63.657	636.619
2	0.816	1.886	2.920	4.303	6.965	9.925	31.598
3	0.765	1.638	2.353	3.182	4.541	5.841	12.941
4	0.741	1.533	2.132	2.776	3.747	4.604	8.610
5	0.727	1.476	2.015	2.571	3.365	4.032	6.859
6	0.718	1.440	1.943	2.447	3.143	3.707	5.959
7	0.711	1.415	1.895	2.365	2.998	3.499	5.405
8	0.706	1.397	1.860	2.306	2.896	3.355	5.041
9	0.703	1.383	1.833	2.262	2.821	3.250	4.781
10	0.700	1.372	1.812	2.228	2.764	3.169	4.587
11	0.697	1.363	1.796	2.201	2.718	3.106	4.437
12	0.695	1.356	1.782	2.179	2.681	3.055	4.318
13	0.694	1.350	1.771	2.160	2.650	3.012	4.221
14	0.692	1.345	1.761	2.145	2.624	2.977	4.140
15	0.691	1.341	1.753	2.131	2.602	2.947	4.073
16	0.690	1.337	1.746	2.120	2.583	2.921	4.015
17	0.689	1.333	1.740	2.110	2.567	2.898	3.965
18	0.688	1.330	1.734	2.101	2.552	2.878	3.922
19	0.688	1.328	1.729	2.093	2.539	2.861	3.883
20	0.687	1.325	1.725	2.086	2.528	2.845	3.850
21	0.686	1.323	1.721	2.080	2.518	2.831	3.819
22	0.686	1.321	1.717	2.074	2.508	2.819	3.792
23	0.685	1.319	1.714	2.069	2.500	2.807	3.767
24	0.685	1.318	1.711	2.064	2.492	2.797	3.745
25	0.684	1.316	1.708	2.060	2.485	2.787	3.725
26	0.684	1.315	1.706	2.056	2.479	2.779	3.707
27	0.684	1.314	1.703	2.052	2.473	2.771	3.690
28	0.683	1.313	1.701	2.048	2.467	2.763	3.674
29	0.683	1.311	1.699	2.045	2.462	2.756	3.659
30	0.683	1.310	1.697	2.042	2.457	2.750	3.646
40	0.681	1.303	1.684	2.021	2.423	2.704	3.551
60	0.679	1.296	1.671	2.000	2.390	2.660	3.460
120	0.677	1.289	1.658	1.980	2.358	2.617	3.373
∞	0.674	1.282	1.645	1.960	2.326	2.576	3.291

Source: Adapted from Morrison [2].

- (6) The equation of the sample regression line is therefore

$$\hat{Y} = 13.63 - 0.08X$$

The value of b indicates that a 1°F increase in average monthly temperature has been associated with an average decrease of 0.08 pound of steam used. A plot of the regression line appears in Figure B-3. It is not meaningful to interpret the value of the sample intercept (a) for these data, since no X 's were observed near 0. The predicted amount of steam used in a month with average temperature, X , of 50°F is given by

$$\begin{aligned}\hat{Y} &= 13.63 - 0.08(50) \\ &= 9.63 \text{ lb/mo}\end{aligned}$$

- (7) The residual for the first observation in Table B-1 is

$$\begin{aligned}Y_1 - \hat{Y}_1 &= Y_1 - a - bX_1 \\ &= 10.98 - 13.63 - (-.08)(35.3) \\ &= 0.17\end{aligned}$$

- (8) From Eq. B-7,

$$\begin{aligned}s_{Y \cdot X} &= \sqrt{\frac{n-1}{n-2} (s_Y^2 - b^2 s_X^2)} \\ &= \sqrt{\frac{24}{23} [1.63^2 - (.08^2)(17.27^2)]} \\ &= 0.88\end{aligned}$$

When the basic assumptions for a regression analysis are satisfied, two thirds of the observed Y values should lie within $\pm s_{Y \cdot X}$ of the sample regression line.

- (9) The estimated standard errors of a and b (Eqs. B-11 and B-12) are:

$$\begin{aligned}\text{s.e. (a)} &= .88 \sqrt{\frac{1}{25} + \frac{52.6^2}{24(17.27^2)}} \\ &= 0.57\end{aligned}$$

and

$$\begin{aligned}\text{s.e. (b)} &= \sqrt{\frac{0.88^2}{(24)(17.27^2)}} \\ &= 0.010\end{aligned}$$

- (10) Both 90% and 95% confidence intervals for B will be calculated. The only difference in the calculations is the value of t that is used in Eq. B-13. For

a 90% confidence interval, $\alpha = 0.10$ and $(1 - \alpha/2) = 0.95$. From Table B-2, the 95th percentile of the t-distribution with $n - 2 = 23$ degrees of freedom is found to be 1.714. Therefore,

$$\begin{aligned} B_L &= b - t_{.95}(23) \text{ s.e. } (b) \\ &= -0.080 - 1.714 (0.010) \\ &= -0.097 \end{aligned}$$

(11) Similarly,

$$\begin{aligned} B_U &= -0.080 + 1.714 (0.010) \\ &= -0.063 \end{aligned}$$

(12) Thus, with 90% confidence, one can assert that B is between -0.097 and -0.063 , or that a 90% confidence interval for B is $(-0.097, -0.063)$. While the exact value of B is not known and may fall outside of the interval, 90% of all confidence intervals that are calculated using this method will contain B.

(13) To calculate a 95% confidence interval, use the 97.5th percentile of t with 23 degrees of freedom. From Table B-2, this number is 2.069. Using the same procedure as above, the 95% confidence interval for B is $(-0.101, -.059)$. This interval is, of course, larger than the 90% confidence interval because of the increased confidence that it will contain B.

(14) A confidence interval for A is not of substantive interest for this example. To demonstrate the calculation, however, the 95% confidence interval will be found. From Eq. B-14, the limits are:

$$\begin{aligned} A_L &= 13.63 - 2.069 (0.57) \\ &= 12.4 \end{aligned}$$

and

$$A_U = 14.8$$

The 95% confidence interval for A is therefore (12.4, 14.8).

The value of A can be interpreted as the average response (Y) for units with $X = 0$. If the X's are all far from 0, as they are here, the value of A is of no practical importance.

B-4 EVALUATING THE REGRESSION

After finding the point estimates and possibly confidence intervals for A and B, it is often instructive to evaluate formally how well the proposed linear relationship describes the data at hand. This evaluation may consist of different steps, depending on individual needs:

- (1) investigating again the appropriateness of the assumptions in Section B-2;

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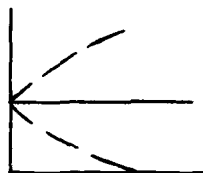
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- (2) calculating a summary statistic (R^2) which tells what proportion of the variation in Y has been explained by the sample regression;
- (3) testing formally whether there is indeed a linear relationship between X and Y, i.e., is b significantly different from 0?

Steps to ascertain that the assumptions for this analysis are valid should always be done. The steps outlined here depend on the sample residuals ($Y_i - \hat{Y}_i$); this seems reasonable, since most of the assumptions deal with properties of the errors. Again the use of scatterplots is recommended, since most problems are easily seen this way. Several plots are listed along with a description of the desired appearance and problems that may be seen. As many of these plots as are pertinent and possible should be made.

1. *Histogram of residuals.* Should be fairly symmetrical and centered at 0. Outliers or other signs of non-normality may show up. (Example provided in Figure B-4.)
2. *Probability plot of residuals.* Should be approximately a straight line. Curves or straggling ends indicate a non-normal distribution of errors. (Example provided in Figure B-5.)
3. *Residuals versus \hat{Y}_i , called residuals versus predicted,* should look random with no pattern. Curves or other trends indicate a nonlinear relationship or nonindependent errors. A megaphone shape (as shown below)



or other uneven spread indicates heterogeneous variance. (Example of residuals versus predicted plot given in Figure B-6a.)

4. *Residuals versus order of observation* should be random. Any pattern or trend indicates systematic variation in Y across time and leads to nonindependent errors. (Example in Figure B-6b.)
5. *Residuals versus operator, temperature, day, etc.* (any quantities which varied as the data were observed); trends indicate nonindependent errors or the need for other variables

in the regression. Uneven spread indicates heteroscedastic variances.

Remedies for these problems do exist, but a detailed discussion is beyond the scope of this discussion. Multiple linear regression allows use of additional predictor variables. Transformations of X and/or polynomial regression are helpful for nonlinearity. Transformations of Y may solve non-normality or heteroscedasticity problems. Weighted least-squares may be done to account for heteroscedastic variances. These topics are discussed in Draper and Smith [1] and other statistics books. It may be necessary to consult with a statistician.

Steps (2) and (3) in the evaluation both depend on an analysis of variance of the sample data. The rationale behind the analysis of variance is that the total variation in Y,

$$\sum_{i=1}^n (Y_i - \bar{Y})^2$$

can be split into two components: the variation explained by the regression,

$$\sum_{i=1}^n (\hat{Y}_i - \bar{Y})^2$$

and the residual or unexplained variation, which is

$$\sum_{i=1}^n (Y_i - \hat{Y}_i)^2$$

Each of the quantities is called a "sum of squares," and the relationship

$$\begin{array}{l} \text{Total (corrected) sum of squares =} \\ \text{(SST)} \\ \text{Sum of squares due to regression + Error sum of squares} \\ \text{(SSR) \hspace{10em} (SSE)} \end{array} \quad \text{(B-15)}$$

will always hold.

Results of an analysis of variance are usually displayed in an analysis of variance (ANOVA) table as shown in Table B-3. Computing formulas for the various quantities are also given. Each mean square is the sum of squares divided by the corresponding degrees of freedom.

TABLE B-3

Analysis of Variance (ANOVA) Table

Source	Sum of Squares	Degrees of Freedom	Mean Square
Regression	$SSR = (n - 1) b^2 s_X^2$	1	$MSR = SSR$
Error	$SSE = (n - 2) s_{Y \cdot X}^2$	$n - 2$	$MSE = s_{Y \cdot X}^2$
Total	$SST = (n - 1) s_Y^2$	$n - 1$	s_Y^2

From the ANOVA table, one can complete steps (2) and (3) of the evaluation. The squared multiple correlation coefficient (R^2) is the proportion of the total sum of squares that has been explained by the sample regression. From the ANOVA table we see that

$$R^2 = \frac{SSR}{SST} = \frac{b^2 s_X^2}{s_Y^2} \quad (B-16)$$

Obviously, R^2 lies between 0 and 1. The value of R^2 may be distorted by the presence of outliers or by small sample size; its significance should be interpreted cautiously in these cases. Otherwise, a large value of R^2 indicates that simple linear regression does a good job of explaining the observed variability in Y . R^2 is the square of r , the simple correlation coefficient between X and Y . The correlation coefficient

$$r = \frac{bs_X}{s_Y} \quad (B-17)$$

lies between -1 and $+1$, depending on the sign of b and the degree of linearity in the relationship.

At times, it is important to decide formally whether the data support the existence of a linear relationship between X and Y . In statistical jargon, one wishes to test the null hypothesis $H_0: B = 0$ versus the alternative hypothesis $H_A: B \neq 0$. The rationale guiding this procedure stems from the fact that even if $B = 0$, the computed value of b will seldom, if ever, be zero. How far away from 0 must b lie before one has confidence that $B \neq 0$? The answer to this question depends on the sample size, n , the variability of the X 's as measured by $(n - 1)s_X^2$, and the risk one is willing to take of erroneously deciding $B \neq 0$ when it really is. The risk level, or level of significance, is usually set at 10%, 5%, or 1%, depending on the seriousness of an error.

The procedure for testing $H_0: B = 0$ is given below.

- (1) Choose the significance level (α).
- (2) Calculate the test statistic

$$F = \frac{MSR}{MSE} \quad (B-18)$$

using values of MSR and MSE from Table B-3.

- (3) Locate the comparison value of the F-distribution in Table B-4. The appropriate value depends on the degrees of freedom for the numerator (m) and the denominator (k) of the F statistic (Eq. B-18). These degrees of freedom are found in the ANOVA table (Table B-3) as $m = 1$ and $k = n - 2$. Therefore, the appropriate comparison value is $F_{1-\alpha}(1, n - 2)$.
- (4) Compare F with $F_{1-\alpha}(1, n - 2)$:
 - If $F \geq F_{1-\alpha}(1, n - 2)$, reject H_0 ; conclude $B \neq 0$.
 - If $F < F_{1-\alpha}(1, n - 2)$, do not reject H_0 ; observed b is not significantly different from 0.

An alternative but equivalent test is based on the t-distribution:

- (1) Choose α .
- (2) Calculate

$$t = \left| \frac{b}{s.e.(b)} \right| \quad (B-19)$$

using Eq. B-12 for s.e.(b).

- (3) Find $t_{1-\alpha/2}(n - 2)$ in Table B-2.
- (4) If $t \geq t_{1-\alpha/2}(n - 2)$, reject H_0 .
If $t < t_{1-\alpha/2}(n - 2)$, do not reject H_0 .

Some researchers choose to report the results of their hypothesis tests in a different manner. Rather than saying they have rejected or failed to reject $H_0: B = 0$, they report a p-value, which is a measure of the plausibility of the null hypothesis. A p-value is the smallest significance level for which the null hypothesis would be rejected. To find a p-value, find in Table B-2 or B-4 the largest $F(1, n - 2)$ or $t(n - 2)$ which is

TABLE B-4

Upper Percentage Points of the F Distribution

$1 - \alpha$	$k \backslash m$	1	2	3	4	5
0.90	1	39.9	49.5	53.6	55.8	57.2
0.95		161	200	216	225	230
0.975		648	800	864	900	922
0.99		4,050	5,000	5,400	5,620	5,760
0.995		16,200	20,000	21,600	22,500	23,100
0.90	2	8.53	9.00	9.16	9.24	9.29
0.95		18.5	19.0	19.2	19.2	19.3
0.975		38.5	39.0	39.2	39.2	39.3
0.99		98.5	99.0	99.2	99.2	99.3
0.995		199	199	199	199	199
0.90	3	5.54	5.46	5.39	5.34	5.31
0.95		10.1	9.55	9.28	9.12	9.01
0.975		17.4	16.0	15.4	15.1	14.9
0.99		34.1	30.8	29.5	28.7	28.2
0.995		55.6	49.8	47.5	46.2	45.4
0.90	4	4.54	4.32	4.19	4.11	4.05
0.95		7.71	6.94	6.59	6.39	6.26
0.975		12.2	10.6	9.98	9.60	9.36
0.99		21.2	18.0	16.7	16.0	15.5
0.995		31.3	26.3	24.3	23.2	22.5
0.90	5	4.06	3.78	3.62	3.52	3.45
0.95		6.61	5.79	5.41	5.19	5.05
0.975		10.0	8.43	7.76	7.39	7.15
0.99		16.3	13.3	12.1	11.4	11.0
0.995		22.8	18.3	16.5	15.6	14.9
0.90	6	3.78	3.46	3.29	3.18	3.11
0.95		5.99	5.14	4.76	4.53	4.39
0.975		8.81	7.26	6.60	6.23	5.99
0.99		13.7	10.9	9.78	9.15	8.75
0.995		18.6	14.5	12.9	12.0	11.5
0.90	7	3.59	3.26	3.07	2.96	2.88
0.95		5.59	4.74	4.35	4.12	3.97
0.975		8.07	6.54	5.89	5.52	5.29
0.99		12.2	9.55	8.45	7.85	7.46
0.995		16.2	12.4	10.9	10.1	9.52
0.90	8	3.46	3.11	2.92	2.81	2.73
0.95		5.32	4.46	4.07	3.84	3.69
0.975		7.57	6.06	5.42	5.05	4.82
0.99		11.3	8.65	7.59	7.01	6.63
0.995		14.7	11.0	9.60	8.81	8.30
0.90	9	3.36	3.01	2.81	2.69	2.61
0.95		5.12	4.26	3.86	3.63	3.48
0.975		7.21	5.71	5.08	4.72	4.48
0.99		10.6	8.02	6.99	6.42	6.06
0.995		13.6	10.1	8.72	7.96	7.47

(Continued)

TABLE B-4 (Continued)

$1 - \alpha$	$k \backslash m$	1	2	3	4	5
0.90	10	3.29	2.92	2.73	2.61	2.52
0.95		4.96	4.10	3.71	3.48	3.33
0.975		6.94	5.46	4.83	4.47	4.24
0.99		10.0	7.56	6.55	5.99	5.64
0.995		12.8	9.43	8.08	7.34	6.87
0.90	12	3.18	2.81	2.61	2.48	2.39
0.95		4.75	3.89	3.49	3.26	3.11
0.975		6.55	5.10	4.47	4.12	3.89
0.99		9.33	6.93	5.95	5.41	5.06
0.995		11.8	8.51	7.23	6.52	6.07
0.90	15	3.07	2.70	2.49	2.36	2.27
0.95		4.54	3.68	3.29	3.06	2.90
0.975		6.20	4.77	4.15	3.80	3.58
0.99		8.68	6.36	5.42	4.89	4.56
0.995		10.8	7.70	6.48	5.80	5.37
0.90	20	2.97	2.59	2.38	2.25	2.16
0.95		4.35	3.49	3.10	2.87	2.71
0.975		5.87	4.46	3.86	3.51	3.29
0.99		8.10	5.85	4.94	4.43	4.10
0.995		9.94	6.99	5.82	5.17	4.76
0.90	30	2.88	2.49	2.28	2.14	2.05
0.95		4.17	3.32	2.92	2.69	2.53
0.975		5.57	4.18	3.59	3.25	3.03
0.99		7.56	5.39	4.51	4.02	3.70
0.995		9.18	6.35	5.24	4.62	4.23
0.90	60	2.79	2.39	2.18	2.04	1.95
0.95		4.00	3.15	2.76	2.53	2.37
0.975		5.29	3.93	3.34	3.01	2.79
0.99		7.08	4.98	4.13	3.65	3.34
0.995		8.49	5.80	4.73	4.14	3.76
0.90	120	2.75	2.35	2.13	1.99	1.90
0.95		3.92	3.07	2.68	2.45	2.29
0.975		5.15	3.80	3.23	2.89	2.67
0.99		6.85	4.79	3.95	3.48	3.17
0.995		8.18	5.54	4.50	3.92	3.55
0.90	∞	2.71	2.30	2.08	1.94	1.85
0.95		3.84	3.00	2.60	2.37	2.21
0.975		5.02	3.69	3.12	2.79	2.57
0.99		6.63	4.61	3.78	3.32	3.02
0.995		7.88	5.30	4.28	3.72	3.35

Source: Adapted from Morrison [2]

smaller than the calculated t or F and report the observed significance level. (More details are given in the example below.) All the procedures described in this section are now demonstrated using the data from Table B-1.

Example B-2 Evaluating the regression.

- (1) First the residuals, $Y_i - \hat{Y}_i$, are examined. Table B-5 contains the X value, predicted value (\hat{Y}_i), and residual for each observation. A histogram of the residuals is given in Figure B-4.

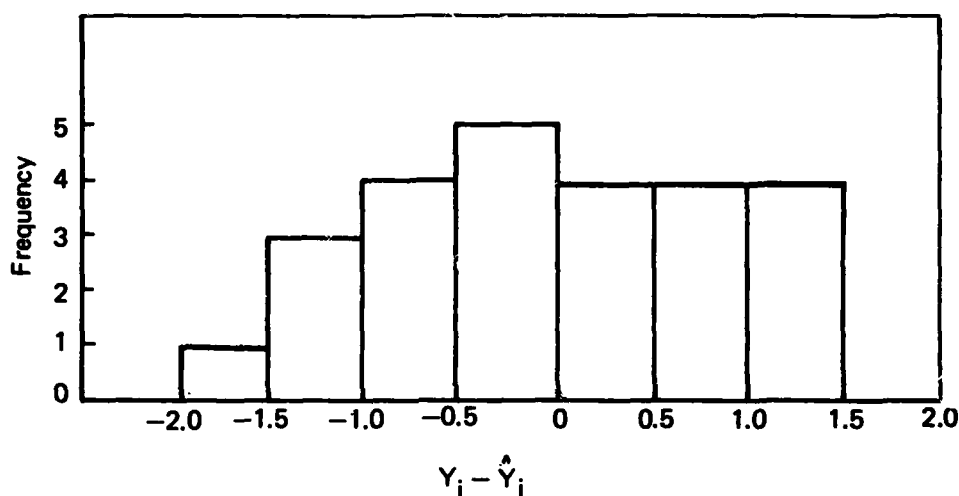


FIGURE B-4 Histogram of Residuals

The histogram does not show any obvious outliers; it does, however, indicate too many large residuals. With only 25 observations, a sample histogram may deviate strongly from a normal shape before giving firm evidence that the underlying distribution is non-normal. A normal probability plot of the residuals, in Figure B-5, shows some curvature, but the basic pattern is linear. This same pattern, with a larger sample, would cause one to consider corrective measures, perhaps a transformation of Y .

- (2) Figure B-6 shows two other residual plots which should be routinely done, if possible. Neither of these plots displays any obvious pattern. If values of other variables were available for these units, residual plots should be made for these variables also.
- (3) Since no alarming deviations were found in the previous steps, it is appropriate to continue. The analysis of variance for these data is in Table B-6.

TABLE B-5

Predicted Values and Residuals

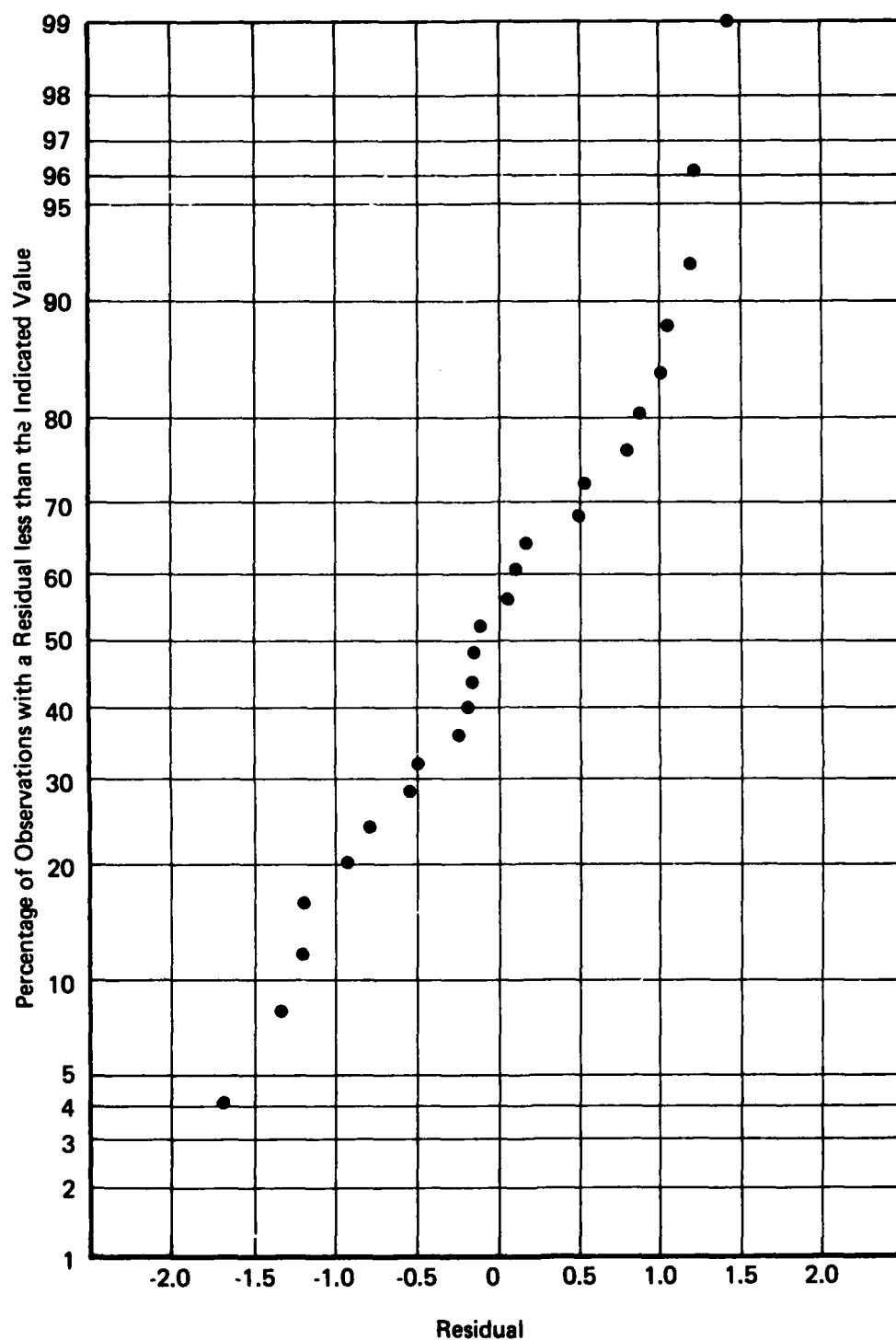
Observation Number	X	\hat{Y}	$Y - \hat{Y}$
1	35.3	10.81	0.17
2	29.7	11.25	-0.12
3	30.8	11.17	1.34
4	58.8	8.93	-0.53
5	61.4	8.72	0.55
6	71.3	7.93	0.80
7	74.4	7.68	-1.32
8	76.7	7.50	1.00
9	70.7	7.98	-0.16
10	57.5	9.03	0.11
11	46.4	9.92	-1.68
12	28.9	11.32	0.87
13	28.1	11.38	0.50
14	39.1	10.50	-0.93
15	46.8	9.89	1.05
16	48.5	9.75	-0.17
17	59.3	8.89	1.20
18	70.0	8.04	0.07
19	70.0	8.04	-1.21
20	74.5	7.68	1.20
21	72.1	7.87	-0.19
22	58.1	8.98	-0.51
23	44.6	10.06	-1.20
24	33.4	10.96	-0.60
25	28.6	11.34	-0.26

Source: Adapted from Draper and Smith [1], p. 12.

- (4) The squared multiple correlation is calculated with Eq. B-16 as

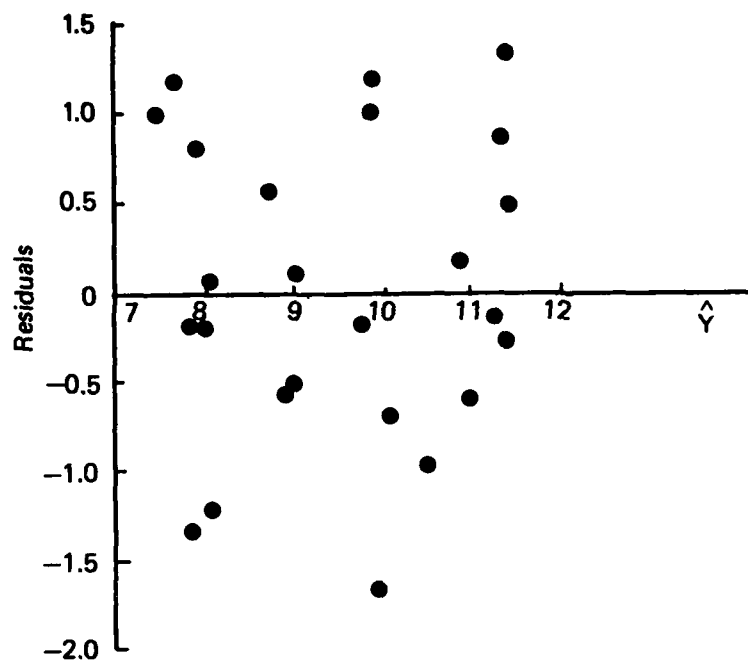
$$R^2 = \frac{45.81}{63.76} = 0.718$$

Thus, the average monthly temperature explains about 72% of the observed variability in pounds of steam used. The other 28% of the variability cannot be explained with this linear regression.

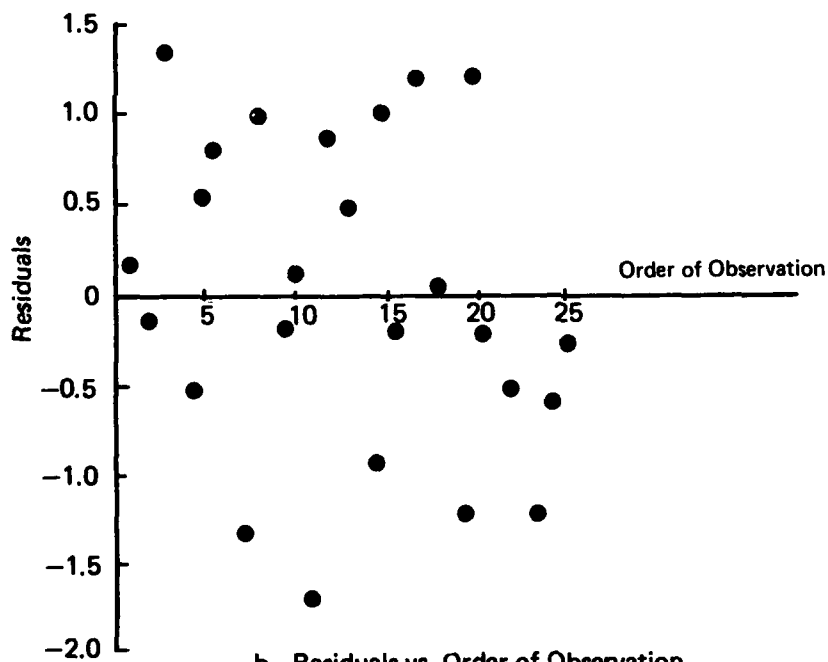


(This plot should be approximately linear when errors follow a normal distribution.)

FIGURE B-5 Normal Probability Plot of Residuals



a. Residuals vs. Predicted Values



b. Residuals vs. Order of Observation

FIGURE B-6 Residual Plots

TABLE B-6

Analysis of Variance

Source	Sum of Squares	Degrees of Freedom	Mean Square
Regression	45.81	1	45.81
Error	<u>17.95</u>	<u>23</u>	.781
Total	63.76	24	2.657

- (5) The procedure for testing $H_0: B = 0$ vs. $H_A: B \neq 0$ will be demonstrated. The significance level $\alpha = .05$ will be used. This means that if the average temperature (X) and pounds of steam used (Y) are actually unrelated, there is a 5% chance of erroneously concluding that they are related. The F-statistic (Eq. B-18) is

$$F = \frac{MSR}{MSE} = \frac{45.81}{0.781} = 58.7$$

It must be compared with $F_{.95}(1, 23)$ from Table B-4. Let $m=1$, $n = 23$, $1 - \alpha = .95$ and find $F_{.95}(1, 23) \cong 4.29$. (As only $n=20$ and $n = 30$ are given in the table, the approximate value is found using linear interpolation.) Since $F = 58.7$ is much larger than 4.29, the null hypothesis is rejected. One concludes that $B \neq 0$; there is a linear relationship between X and Y.

- (6) To test the same hypothesis using the t-distribution, evaluate Eq. B-19:

$$t = \left| \frac{b}{s.e.(b)} \right| = \left| \frac{-0.08}{0.010} \right| = 8.0$$

Compare this with $t_{.975}(23) = 2.069$ from Table B-2. As $8.0 > 2.069$, the same conclusion is reached.

- (7) To find a p-value for this hypothesis, it is necessary to compare the calculated t with several values. From Table B-2, one finds

$$\begin{aligned} t_{0.975}(23) &= 2.069 (\alpha = 0.05) \\ t_{0.99}(23) &= 2.500 (\alpha = 0.02) \\ t_{0.995}(23) &= 2.807 (\alpha = 0.01) \\ t_{0.9995}(23) &= 3.767 (\alpha = 0.001) \end{aligned}$$

Since the calculated $t = 8.0$ is larger than all of these, the approximate p-value is $p < .001$. This is very convincing evidence that $B \neq 0$. Had $t = 2.71$ been observed, one would report $.01 < p < .02$, as 2.71 falls between 2.500 and 2.807.

B-5 PREDICTING FUTURE VALUES OF Y

A common use of the results of a regression analysis is predicting future Y values for known values of X. Since the prediction cannot be exact, it is recommended that one report a prediction interval, analogous to a confidence interval, in addition to the point prediction. Let X_0 be the known value of X for which a prediction is desired. Based on the sample data, the best point prediction for Y at X_0 is the value of the sample regression line:

$$\hat{Y}_{X_0} = a + b X_0 \quad (\text{B-20})$$

The next value of Y observed for $X = X_0$ will not be equal to \hat{Y}_{X_0} for two primary reasons:

- (1) $Y = A + BX$ is the true regression line; $\hat{Y} = a + bX$ is an estimate which is subject to error, because $a \neq A$ and $b \neq B$.
- (2) Observed Y's do not fall exactly on the line $A + BX$ because of random error. The likely magnitude of this error is given by $\sigma_{Y \cdot X}$. If $\sigma_{Y \cdot X}$ is large, accurate point predictions cannot be made.

To account for these errors it is best to report a prediction interval. A prediction interval consists of two numbers P_L and P_U calculated so that the probability that the next Y at X_0 falls between P_U and P_L is $1 - \alpha$. By choosing a small α , one can be quite certain that the value will fall in the prediction interval.

As a preliminary step to calculating the prediction interval, one needs s.e. (\hat{Y}_{X_0}), the estimated standard error of the prediction. This is given by

$$\text{s.e.}(\hat{Y}_{X_0}) = s_{Y \cdot X} \sqrt{1 + \frac{1}{n} + \frac{(X_0 - \bar{X})^2}{(n-1) s_X^2}} \quad (\text{B-21})$$

From Eq. B-21, one sees that predictions will be more accurate for X's near \bar{X} than for those far away. The prediction interval is given by

$$\begin{aligned}
 P_L &= \hat{Y}_{X_0} - t_{1-\alpha/2} (n-2) \text{ s.e. } (\hat{Y}_{X_0}) \\
 \text{and} \\
 P_U &= \hat{Y}_{X_0} + t_{1-\alpha/2} (n-2) \text{ s.e. } (\hat{Y}_{X_0})
 \end{aligned}
 \quad \left. \vphantom{\begin{aligned} P_L \\ P_U \end{aligned}} \right\} \quad (B-22)$$

The t-values may be found in a t-table as described in Section B-3. It is often useful to calculate prediction intervals for several values of X and summarize the results in a graph, as shown in Figure B-7.

A word of warning about the accuracy of prediction intervals: do not make predictions for X's outside the range of the original data. Extrapolation can lead to serious errors. The predictions are based on an assumed linear relationship between X and Y; it is known to be linear only for the X's in the original data set. For larger or smaller X's, the relationship may curve. Figure B-8 displays this difficulty.

Example B-3 Predicting future values of Y.

- (1) It is desired to predict pounds of steam used (Y) for a month with average temperature $X_0 = 43^\circ\text{F}$. The point prediction (from Eq. B-20) is:

$$\begin{aligned}
 \hat{Y}_{43} &= a + b(43) \\
 &= 13.63 - 0.08(43) \\
 &= 10.2
 \end{aligned}$$

- (2) The estimated standard error of the prediction (Eq. B-21) is:

$$\begin{aligned}
 \text{s.e. } (\hat{Y}_{43}) &= s_{Y.X} \sqrt{1 + \frac{1}{n} + \frac{(X_0 - \bar{X})^2}{(n-1)s_X^2}} \\
 &= 0.8835 \sqrt{1 + \frac{1}{25} + \frac{(43 - 52.6)^2}{24(17.27^2)}} \\
 &= 0.9066
 \end{aligned}$$

- (3) A 95% prediction interval is then obtained from Eq. B-22:

$$\begin{aligned}
 P_L &= 10.2 - 2.069(.9066) \\
 &= 8.3
 \end{aligned}$$

and

$$\begin{aligned}
 P_U &= 10.2 + 2.069(.9066) \\
 &= 12.1
 \end{aligned}$$

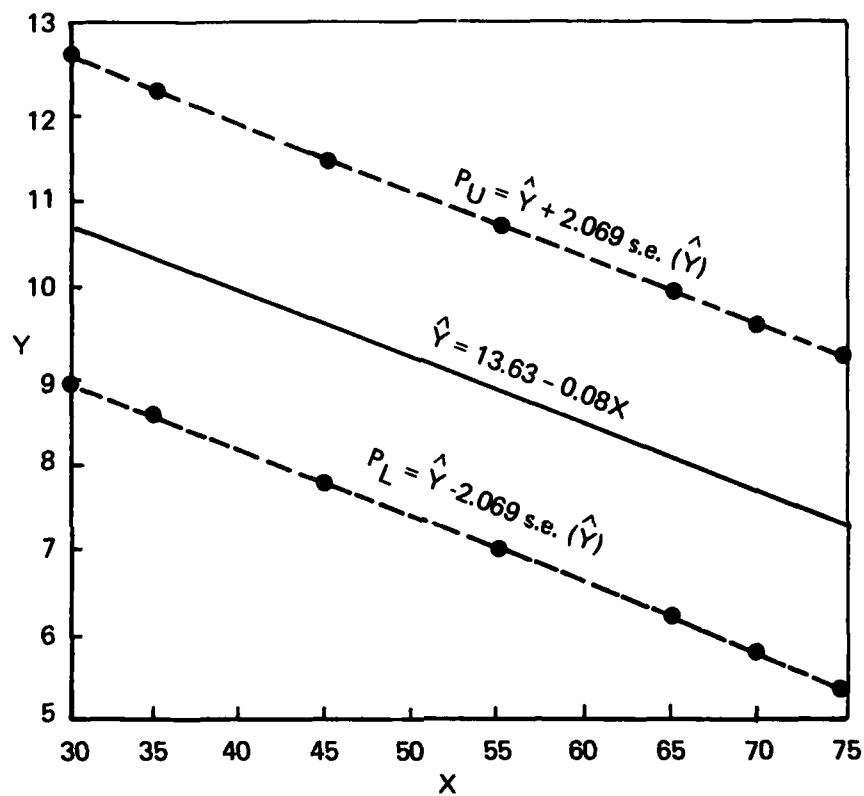


FIGURE B-7 95% Prediction Intervals

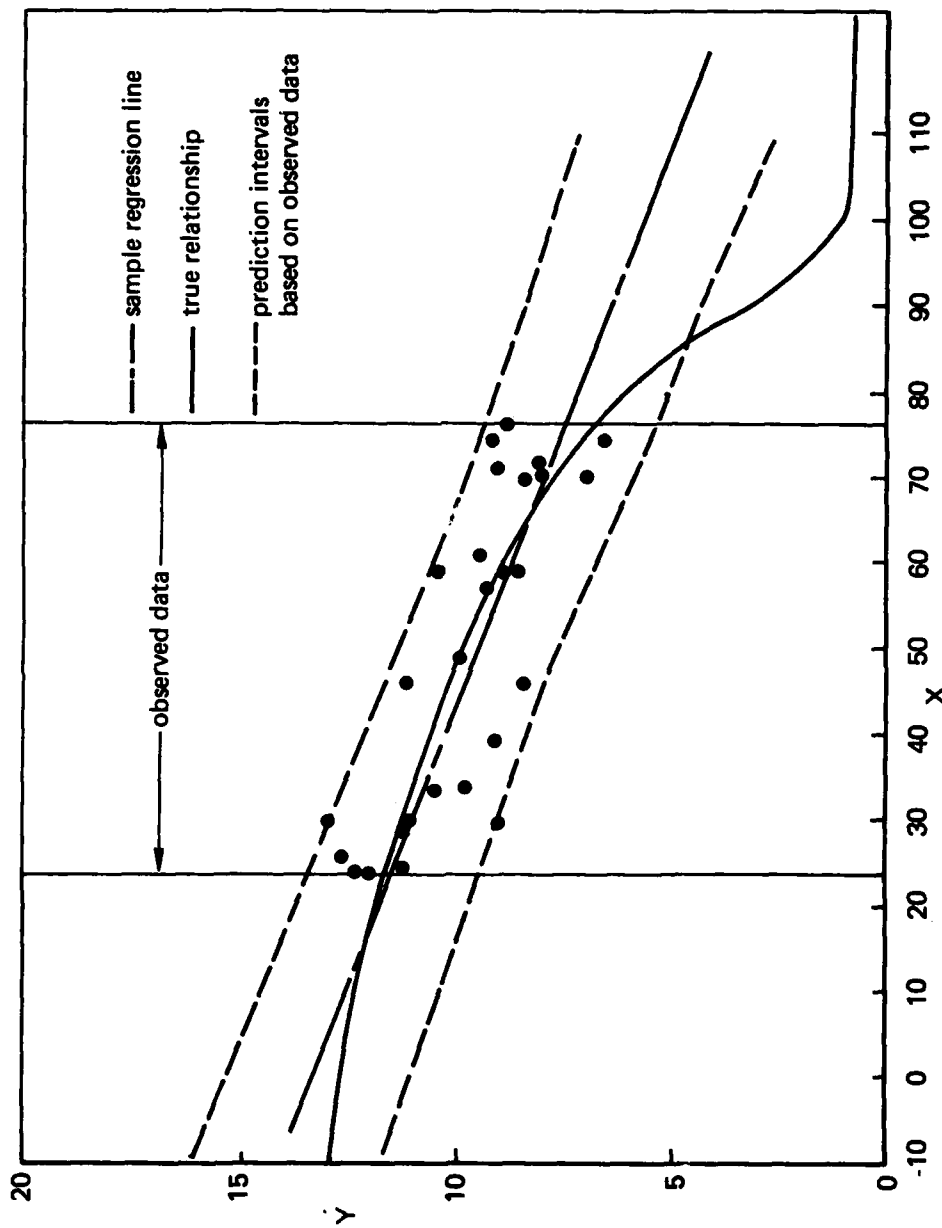


FIGURE B-8 Problems with Extrapolation

Thus, with probability of 95%, the pounds of steam used in a month with average temperature of 43° (\hat{Y}_{43}) will be between 8.3 and 12.1. Ninety-five percent prediction intervals are given in Table B-7 for several X 's. The results were previously shown in Figure B-7.

TABLE B-7

95% Prediction Intervals			
X_0	\hat{Y}	P_L	P_U
30	10.83	8.90	12.76
35	10.43	8.53	12.33
45	9.63	7.76	11.50
55	8.83	6.97	10.69
65	8.03	6.15	9.91
70	7.63	5.73	9.53
75	7.23	5.30	9.16
80	6.83	4.87	8.78

B-6 SYMBOLS USED

A	=	intercept of regression line in Eq. B-1
A_L	=	lower confidence interval for A , Eq. B-14
A_U	=	upper confidence interval for A , Eq. B-14
a	=	estimate of A in Eqs. B-2 and -6
B	=	slope of regression line in Eq. B-1
B_L	=	lower confidence interval for B , Eq. B-13
B_U	=	upper confidence interval for B , Eq. B-13
b	=	estimate of B in Eqs. B-2 and -3
F	=	test statistic in Eq. B-18
H_0	=	null hypothesis
H_A	=	alternative hypothesis
k	=	degrees of freedom for denominator of F statistic
m	=	degrees of freedom for numerator of F statistic
MSR	=	mean square of regression
MSE	=	mean square of error ($= s^2_{\hat{Y}, X}$)
n	=	number of data points in set
P_L	=	lower prediction limit in Eq. B-22
P_U	=	upper prediction limit in Eq. B-22
p	=	("p-value") the smallest significance level for which the null hypothesis would be rejected
R	=	correlation coefficient in Eq. B-16

r	=	simple correlation coefficient between X and Y in Eq. B-17
s_Y^2	=	sample variance of Y in Eq. B-9
s_X^2	=	sample variance of X in Eq. B-8
$s_{Y \cdot X}$	=	estimate of $\sigma_{Y \cdot X}$ in Eqs. B-7 and -10
s.e. (a)	=	estimate of the standard error of a in Eq. B-11
s.e. (b)	=	estimate of the standard error of b in Eq. B-12
s.e. (\hat{Y}_{x_0})	=	estimated standard error of the prediction in Eq. B-21
SSE	=	sum of squares due to error in Eq. B-15
SSR	=	sum of squares due to regression in Eq. B-15
SST	=	total (corrected) sum of squares in Eq. B-15
t	=	observed value of test statistic in Eq. B-19
X	=	predictor or control variable in Eq. B-1
\bar{X}	=	simple mean of X values in Eq. B-4
Y	=	response or dependent variable in Eq. B-1
\bar{Y}	=	simple mean of Y values in Eq. B-5
\hat{Y}	=	predicted value of Y for a given X in Eq. B-2

Greek

α	=	significance level for testing hypotheses or forming confidence intervals
$\sigma_{Y \cdot X}$	=	standard deviation of the errors

B-7 REFERENCES

1. Draper, N.R. and H. Smith, *Applied Regression Analysis*, John Wiley & Sons, New York (1966).
2. Morrison, D.F., *Multivariate Statistical Methods*, 2nd ed., McGraw-Hill Book Co., New York (1976).

C

EVALUATING PROPAGATED AND TOTAL ERROR IN CHEMICAL PROPERTY ESTIMATES

Cathy Campbell

C-1 INTRODUCTION

Using the estimation procedures described in this handbook involves a two-step procedure. First, one obtains chemical-specific input values (and sometimes other parameters and constants) required by the estimation method. Second, these input values are used in an estimation process that yields an estimate of the unknown property of interest.

Assessing the likely error in an estimate is a key component in determining the applicability and usefulness of the estimate. All of the estimation methods are accompanied by available information on the magnitude of the error introduced by using that estimation method, by assuming no error in the input values. In many cases, however, the true error may be larger than the method error because the input values themselves have been estimated or otherwise imprecisely determined.

In this appendix a general procedure for assessing the total error in estimates of chemical properties is presented. This method applies to all estimates that are calculated using estimated or imprecise input values. Section C-2 contains a general description of the components of error in an estimated value which is followed, in Section C-3, with some theoretical concepts. Section C-4 contains three methods for estimating total error, one (Method 1) that applies when the estimation procedure uses a

single estimated input and two (Methods 2 and 3) that apply for estimating total error when the procedure uses more than one estimated input. Method 2 is more exact, but also more complicated, than Method 3. Each method is demonstrated with an example, and further examples are given in Section C-5.

C-2 COMPONENTS OF ERROR

Concepts and procedures for estimating total error are introduced via a specific example that will be used to demonstrate the procedures later. Consider Method 3 for estimating the viscosity of a liquid, η_L , at a given temperature T . The procedure follows from three (or two) equations, earlier given as Eqs. 22-13, 22-16, and 22-17:

$$\hat{\eta}_L^* = \eta_{Lb} \exp \left\{ B_4 \left(\frac{1}{T} - \frac{1}{T_b} \right) \right\} \quad (C-1)$$

$$B_4 = \frac{1}{n} (\Delta H_v - RT) \quad (C-2)$$

$$\Delta H_v = K_F T_b (8.75 + R \ln T_b) \quad (C-3)$$

where

- η_{Lb} = viscosity of the liquid at its boiling temperature, T_b ,
- ΔH_v = heat of vaporization,
- R = gas constant, and
- n and K_F = constants which describe the class of chemicals.

When a procedure such as this is used to estimate a property, responsible scientists will want to assess and report the likely error in these results. Error in $\hat{\eta}_L$, or other estimates, may rise from two sources.

- (1) *Method error* occurs because of approximations or inaccuracies in the prediction equation. The estimates are subject to this error even when the chemical-specific input properties, in this case η_{Lb} , T_b , and K_F , are known quite accurately. Table 22-2 gives some assessment of method error for the procedure described here; the average relative error is 19% and the maximum error is 49%.

*A " " above a property indicates the value is estimated.

- (2) *Propagated error* is introduced because the input values have been estimated or imprecisely determined. For example, if T_b is estimated, then uncertainty about the value of T_b creates additional uncertainty in the estimate of η_L .

To demonstrate the effect of propagated error, data from Example 22-6 will be used. Suppose that η_{Lb} and B_4 are known quite precisely with $\eta_{Lb} = 0.2$ cp and $B_4 = 817$. To estimate η_L when $T = -60^\circ\text{C} = 213$ K, Eq. (C-1) becomes

$$\hat{\eta}_L = 0.2 \exp \left\{ 3.84 \left(1 - \frac{213}{T_b} \right) \right\} \quad (\text{C-4})$$

For different values of T_b , the relationship between $\hat{\eta}_L$ and T_b can be plotted as shown in Figure C-1. If, as in the example, $T_b = 342$ K, then η_L is estimated as 0.85 cp. However, if the value of T_b is known to be subject to a 5% error, then T_b could be as small as 325 K or as large as 359 K. This means, as shown in the figure, that $\hat{\eta}_L$ could be as small as 0.75 cp or as large as 0.95 cp. This uncertainty about $\hat{\eta}_L$ comes from the expected error in T_b and must be considered in addition to the method error. The estimation error that derives solely from errors in the input values will be referred to as propagated error.

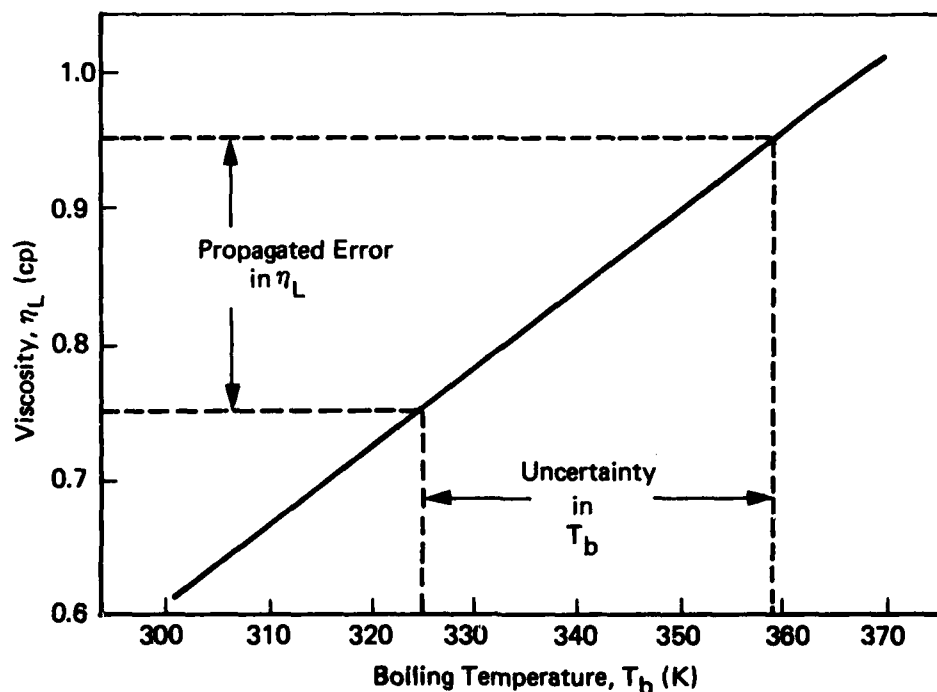


FIGURE C-1 Graph of η_L as a Function of T_b

To realistically assess the total error in $\hat{\eta}_L$, it is necessary to consider both sources of error simultaneously. The procedure given in this chapter leads to evaluating

$$\text{Total Error} = \sqrt{(\text{Method Error})^2 + (\text{Propagated Error})^2} \quad (\text{C-5})$$

For the example given here, if the average method error of 19% is used, and one observes that the propagated error of ± 0.10 is 11.8% of the estimated value, then the total error in the estimate of η_L is approximately 22%.

In this section the concepts of method error, propagated error and total error have been informally introduced for an estimation process that has one input value subject to known error. In the following section, these ideas are described more formally, and the theory of estimating propagated error is briefly presented. The procedure will be extended to estimation methods which have error in more than one input value. Following that, simple and very general procedures for estimating propagated error will be given and demonstrated for a series of examples.

C-3 THEORETICAL BACKGROUND

Some theory for evaluating propagated error and total error is given in this section. First, estimation methods with a single estimated input will be considered. Then procedures for multiple inputs will be developed.

Any of the estimation methods in this handbook give rules for using input characteristics to determine an estimated value of the chemical property. Sometimes, the "rule" can be written down explicitly as an equation or series of equations. The "rule" may consist of a graphical method, such as finding the intersection of two lines or of looking up values in a nomogram. In any case the rule may be expressed as

$$\hat{C} = f(x_o) \quad (\text{C-6})$$

where \hat{C} is the obtained estimate, and x_o is the estimated input value. The function $f(\cdot)$ is the rule linking the input value x_o to the estimated value \hat{C} . In the situation considered here, x_o is an estimate of X_o , the true input value. For instance, X_o may be boiling temperature of a liquid and x_o is the estimated boiling temperature.

The estimate \hat{C} may differ from the true value C because of method error and propagated error. If X_0 is known, then one would calculate $\hat{C} = f(X_0)$ and there would be no propagated error. The difference between $f(X_0)$ and $f(x_0)$ is the propagated error, while the difference between $f(X_0)$ and C , the true value, is method error.

To see the effect of method error and propagated error the estimate may be expressed as

$$\hat{C} = f(x_0) = C + [f(X_0) - C] + [f(x_0) - f(X_0)] \quad (C-7a)$$

or

$$\text{Estimate} = \text{True Value} + \text{Method Error} + \text{Propagated Error} \quad (C-7b)$$

For a particular estimate, the exact values of the method and propagated errors are not known, but using available information about the method error and the likely error in x_0 , one can obtain an average or expected value for the total error.

In the development that follows, both error components are assumed to have an expected value of 0. That is, the differences $f(X_0) - C$ and $f(x_0) - f(X_0)$ may be either positive or negative, but in the long run will average to 0. This assumption will not be satisfied if:

- (1) the method is biased,
- (2) the estimate of X_0 is biased, or
- (3) the rule $f(\cdot)$ has a large second derivative, i.e., the graph of \hat{C} vs. X is curving asymmetrically close to $X = X_0$.

If one also assumes that the magnitude of the method error is independent of the error in x_0 , then one obtains

$$\text{avg. } [(\hat{C} - C)^2] = \text{avg. } [(f(X_0) - C)^2] + \text{avg. } [(f(x_0) - f(X_0))^2] \quad (C-8)$$

or

$$\text{Total Error} = \sqrt{\text{avg. (Method Error)}^2 + \text{avg. (Propagated Error)}^2}, \quad (C-9)$$

where "avg." represents average or expected value. Method, propagated, and total errors may be expressed either in absolute or relative units (error/estimate) so long as consistency is maintained. To evaluate Eq. C-9, one obtains an estimate of error from the literature in the chapters of

this handbook and then uses the procedure given below to estimate propagated error. Theory of propagation of errors has been reviewed by Ku [1]; an outline will be given here.

In Figure C-1, one sees that the change in $\hat{\eta}_L$ when the value of T_b changes is related to the steepness of the graph at the point where T_b changes. Readers who have studied calculus realize that the steepness of a graph at a given point is measured by its first derivative. Although the succeeding development depends on some notation from calculus, the methods for estimating propagated error will not require knowledge of calculus.

If the estimation procedure depends only on a single input which is subject to error, then the estimated error is

$$\text{Propagated Error} = \sqrt{\left[\frac{df}{dX}\right]_{x_0}^2 s_{x_0}^2} \quad (\text{C-10})$$

where $\left[\frac{df}{dX}\right]_{x_0}$ is the first derivative of f evaluated at $X = x_0$, and s_{x_0} is the estimated total error in x_0 .

When the estimation rule can be written explicitly and the derivative easily obtained, then use of Eq. C-10 is the easiest way to evaluate the propagated error. For the example in § C-2, Eq. C-4 gives the rule for estimating η_L for a given value of T_b . [Note that \hat{T}_b corresponds to x_0 and $\eta_L(T_b)$ corresponds to $f(X)$.] The derivative of this function is

$$\frac{d\eta_L(T_b)}{dT_b} = 0.2 \left[\exp\left(3.84 \left(1 - \frac{213}{T_b}\right)\right) \right] \left(\frac{3.84 (213)}{T_b^2} \right) \quad (\text{C-11})$$

When this is evaluated at $\hat{T}_b = 342$, one obtains

$$\left[\frac{d\eta_L}{dT_b}\right]_{\hat{T}_b}^2 = (0.00594)^2 \quad (\text{C-12})$$

It was reported that \hat{T}_b was subject to a 5% error. In absolute units, $s_{\hat{T}_b} = (0.05)(342) = 17.1$. Substituting these values into Eq. C-10 gives propagated error = 0.10, as was found earlier by inspecting the graph.

Other cases, where the graph is more curved, will not necessarily give perfect agreement.

If the estimation rule is a function of p input variables, all of which are subject to error, the propagated error must be evaluated separately for each input variable. The assumption is made that the input values come from difference sources and that the errors in them are independent of each other. Let $\hat{C} = f(X_1, \dots, X_p)$ be the estimation rule, and suppose the rule will be evaluated for numbers (x_1, \dots, x_p) which are estimates of (X_{10}, \dots, X_{p0}) , the "true" values of the input properties. The propagated error is the extent to which $f(x_1, \dots, x_p)$ is expected to differ from $f(X_{10}, \dots, X_{p0})$. Let $(s_{x_1}, \dots, s_{x_p})$ be the estimated errors in (x_1, \dots, x_p) . Then the estimated propagated error is given by

$$\text{Propagated Error} = \sqrt{\sum_{i=1}^p \left[\frac{\partial f}{\partial X_i} \right]_{(x_i)}^2 s_{x_i}^2} \quad (\text{C-13})$$

where $\left[\frac{\partial f}{\partial X_i} \right]_{x_i}$ is partial derivative of f with respect to X_i evaluated at the estimates (x_1, \dots, x_p) .

The following section gives methods for evaluating propagated error that do not depend on having explicit expressions for the derivatives. This approach is somewhat analogous to the graphical approach used in § C-2.

C-4 EVALUATING PROPAGATED ERROR

Single Estimated Input (Method 1). Suppose $C_x = f(X)$ is the estimation rule, and that $\hat{C}_0 = f(X_0)$ is the desired estimate. When X_0 is not known, an estimate x_0 will be used instead. Let s_{x_0} be the estimated error in x_0 . In other words, the estimate of X_0 is $x_0 \pm s_{x_0}$. The estimate of C , then, is $f(x_0)$. The method for evaluating the propagated error consists of using different values in the estimation rule and observing how much the resulting estimate changes.

Basic Steps

- (1) Find $\hat{C}_1 = f(x_0 - s_{x_0})$ by using $x_0 - s_{x_0}$ instead of x_0 in the estimation rule.
- (2) Find $\hat{C}_2 = f(x_0 + s_{x_0})$ by using $x_0 + s_{x_0}$ in the estimation rule.

(3) Estimate the propagated error as

$$\text{Propagated Error} = \sqrt{\frac{(\hat{C}_1 - \hat{C}_2)^2}{4}} \quad (\text{C-14})$$

(4) To estimate the total error in the estimate, a fourth step is to calculate

$$\text{Total Error} = \sqrt{(\text{Method Error})^2 + (\text{Propagated Error})^2} \quad (\text{C-5})$$

Example C-1 In § C-2, Eqs. C-1, -2, and -3 give a rule for estimating liquid viscosity. In the simple example there, it was assumed that B_4 was known. In practice, one estimates ΔH_v from T_b and then estimates B_4 . Thus, T_b is involved in a more complicated fashion than is indicated by Eq. C-4. Again, following Example 22-6, suppose $\eta_{Lb} = 0.2$ cp is known quite precisely, and that $K_F = 1.0$, $R = 1.988$ and $n = 8$. Let $\hat{T}_b = 342\text{K}$ be subject to a 5% error so that $s_{\hat{T}_b} = 17.1\text{K}$. The viscosity estimate is desired for $T = 213\text{K}$.

(1) Evaluate the rule at $\hat{T}_b - s_{\hat{T}_b} = 324.9\text{K}$.

$$\Delta H_v = (1.0)(324.9)[8.75 + 1.988 \ln(324.9)] = 6578$$

$$B_4 = \frac{1}{8} [6578 - (1.988)(213)] = 769.4$$

$$\hat{C}_1 = 0.2 \exp \left\{ 769.4 \left(\frac{1}{213} - \frac{1}{324.9} \right) \right\} = 0.694 \text{ cp}$$

(2) Evaluate the rule at $\hat{T}_b + s_{\hat{T}_b} = 359.1\text{K}$

$$\Delta H_v = (1.0)(359.1)[8.75 + 1.988 \ln(359.1)] = 7342$$

$$B_4 = \frac{1}{8} [7342 - (1.988)(213)] = 864.9$$

$$\hat{C}_2 = 0.2 \exp \left\{ 864.9 \left(\frac{1}{213} - \frac{1}{359.1} \right) \right\} = 1.043 \text{ cp}$$

$$(3) \text{ Propagated Error} = \sqrt{\frac{(0.694 - 1.043)^2}{4}} = 0.175 \text{ cp}$$

(4) Recalling that the average method error is 19% of the true value, the estimated error, in absolute units, is obtained by multiplying the relative error by the estimated viscosity $\hat{\eta}_L = 0.85$.

$$\text{Method Error} = 0.19(0.85 \text{ cp}) = 0.162 \text{ cp}$$

$$\text{Total Error} = \sqrt{(0.163)^2 + (0.175)^2} = 0.238 \text{ cp}$$

In relative terms, estimated total error is 28% of the estimated value.

Multiple Input Values (Method 2). If the estimation rule depends on more than one estimated input, then propagated error must be estimated separately for each estimated input variable. The separate estimates are combined as shown in Eq. C-15. Suppose that $\hat{C} = f(x_1, \dots, x_p)$ is the estimate with (x_1, \dots, x_p) being the available estimates of (X_{10}, \dots, X_{p0}) . Let $(s_{x_1}, \dots, s_{x_p})$ be the estimate of total error in (x_1, \dots, x_p) . The estimate of propagated error is given by

$$\text{Propagated Error} = \sqrt{\sum_{i=1}^p (\text{Propagated Error for Input } i)^2} \quad (\text{C-15})$$

Total Error is found from Eq. C-5 as before.

To find the propagated error for the first input,

- (1) Find $\hat{C}_{11} = f(x_1 - s_{x_1}, x_2, \dots, x_p)$ by using $x_1 - s_{x_1}$ in the estimation rule, but leaving all the other quantities at their original values.
- (2) Find $\hat{C}_{12} = f(x_1 + s_{x_1}, x_2, \dots, x_p)$ by using $x_1 + s_{x_1}$ in the rule with the other values unchanged.

$$(3) \text{ Propagated Error for Input 1} = \sqrt{\frac{(\hat{C}_{11} - \hat{C}_{12})^2}{4}} \quad (\text{C-16})$$

These three steps are repeated for each input. For the last variable the procedure is

- (1) Find $\hat{C}_{p1} = f(x_1, \dots, x_{p-1}, x_p - s_{x_p})$.
- (2) Find $\hat{C}_{p2} = f(x_1, \dots, x_{p-1}, x_p + s_{x_p})$.

$$(3) \text{ Propagated Error for Input } p = \sqrt{\frac{(\hat{C}_{p1} - \hat{C}_{p2})^2}{4}} \quad (\text{C-17})$$

Finally, Eqs. C-15 and -5 can be used to find the propagated and total error. A summary of the steps is given below.

Basic Steps

- (1) Evaluate the propagated error for each input as:

$$\text{Propagated Error for Input } i = \sqrt{\frac{(\hat{C}_{i1} - \hat{C}_{i2})^2}{4}} \quad (\text{C-18})$$

(2) Use Eq. C-15 to find the overall propagated error.

(3) Use Eq. C-5 to find total error.

Continuation of Example C-1 Suppose now that η_{Lb} has been estimated as 0.2 cp with a 10% error, so, $s_{\hat{\eta}_{Lb}} = 0.02$ cp. The estimate $\hat{\eta}_L = f(\hat{T}_b, \hat{\eta}_{Lb})$ now depends on two estimated inputs.

- (1) To find the propagated error for input 1 (\hat{T}_b), one finds $\hat{C}_{11} = f(\hat{T}_b - s_{\hat{T}_b}, \hat{\eta}_{Lb})$ and $\hat{C}_{12} = f(\hat{T}_b + s_{\hat{T}_b}, \hat{\eta}_{Lb})$. That is, for \hat{C}_{11} , substitute $T_b = 324.9$ and $\eta_{Lb} = 0.20$ in Eqs. C-1 to -3. For \hat{C}_{12} , use $T_b = 359.1$ and $\eta_{Lb} = 0.20$. These have already been found in steps (1) and (2) of the previous example which evaluated the error propagated by errors in T_b . The results were

$$\hat{C}_{11} = 0.694 \text{ cp and}$$

$$\hat{C}_{12} = 1.043 \text{ cp,}$$

so,

$$\text{Propagated Error for Input 1} = \sqrt{\frac{(0.694 - 1.043)^2}{4}} = 0.175 \text{ cp}$$

- (2) To find the propagated error for input 2 ($\hat{\eta}_{Lb}$), one needs $\hat{C}_{21} = f(\hat{T}_b, \hat{\eta}_{Lb} - s_{\hat{\eta}})$ and $\hat{C}_{22} = f(\hat{T}_b, \hat{\eta}_{Lb} + s_{\hat{\eta}})$. To find \hat{C}_{21} , evaluate the estimation rule with $T_b = 342K$ and $\eta_{Lb} = 0.18$ cp:

$$\Delta H_v = (1.0) (342) [8.75 + 1.988 \ln (342)] = 6960$$

$$B_4 = \frac{1}{8} [6960 - 1.988 (213)] = 817.0$$

$$\hat{C}_{21} = 0.18 \exp \left\{ 817.0 \left(\frac{1}{213} - \frac{1}{342} \right) \right\} = 0.765$$

Since η_{Lb} does not enter the exponent, \hat{C}_{22} can be found by reevaluating Eq. C-1 with $\eta_{Lb} = 0.22$. Thus,

$$\hat{C}_{22} = 0.22 \exp \left\{ 817.0 \left(\frac{1}{213} - \frac{1}{342} \right) \right\} = 0.935$$

which is found by using $\hat{\eta}_{Lb} + s_{\hat{\eta}}$ in the estimation rule. Now, using Eq. C-18:

$$\text{Propagated Error for Input 2} = \sqrt{\frac{(0.765 - 0.935)^2}{4}} = 0.085 \text{ cp}$$

- (3) Using Eq. C-15,

$$\text{Propagated Error} = \sqrt{0.175^2 + 0.085^2} = 0.194 \text{ cp}$$

- (4) From Step (4) of the previous example, method error was estimated to be 0.162 cp, therefore:

$$\text{Total Error} = \sqrt{0.162^2 + 0.194^2} = 0.253 \text{ cp}$$

The total error is 30% of the estimated value of 0.85 cp.

Simplified Method for Multiple Inputs (Method 3). When the estimation process is difficult, it may be quite burdensome to estimate propagated error. The above examples show, however, that the method error may be a substantial understatement of the total error in the estimate. In the previous example, use of method error alone leads to a 35% understatement of the total error. Therefore some effort to estimate total error seems justified.

The process for estimating propagated error can be simplified somewhat, with a concurrent loss in the accuracy of the estimated error. The simplification may be worthwhile, however, when there are several input values, or if the estimation process is difficult. The simplified process requires that only one extra estimate, rather than two, be calculated for each input. In the previous method, propagated error for an input was estimated by looking at the difference between two estimates that were obtained by changing the value of that input — once by increasing it and once by decreasing it. Thus,

$$\text{Propagated Error for Input } i = \sqrt{\frac{(\hat{C}_{i1} - \hat{C}_{i2})^2}{4}} \quad (\text{C-18})$$

The effect of changing the input can also be estimated by changing the input only once and seeing how far the estimate moves from its original value \hat{C} . Either of the quantities given below can also be used as an estimate of propagated error:

$$\text{Propagated Error for Input } i = |\hat{C}_{i1} - \hat{C}| \quad (\text{C-19})$$

or

$$\text{Propagated Error for Input } i = |\hat{C}_{i2} - \hat{C}| \quad (\text{C-20})$$

For the examples here, $|\hat{C}_{i1} - \hat{C}|$ will be used.

Basic Steps

- (1) Find $\hat{C}_{i1} = f(x_1 - s_{x_1}, x_2, \dots, x_p)$ by using $x_1 - s_{x_1}$ in the estimation rule, but leaving all the other quantities at their original values.

- (2) Calculate Propagated Error for Input 1 using Eq. C-19.
- (3) Repeat steps (1) and (2) for each input (2, . . . , p), each time using $x_i - s_{x_i}$ while leaving the other quantities at their original estimated value.
- (4) Evaluate Propagated Error using Eq. C-15.
- (5) Evaluate Total Error using Eq. C-5.

Example of Simplified Method. (Continuation of Example C-1.) In this example $\hat{C} = 0.85$ cp was the estimate actually obtained for η_L . From the above, it was found that

$$\hat{C}_{11} = 0.694 \text{ cp } [f(\hat{T}_b - s_{T_b}^{\wedge}, \hat{\eta}_{Lb})]$$

and

$$\hat{C}_{21} = 0.765 \text{ cp } [f(\hat{T}_b, \hat{\eta}_{Lb} - s_{\eta_{Lb}}^{\wedge})]$$

Thus,

$$\text{Propagated Error for Input 1} = |0.694 - 0.85| = 0.156 \text{ cp}$$

$$\text{Propagated Error for Input 2} = |0.765 - 0.85| = 0.085 \text{ cp}$$

$$\text{Propagated Error} = \sqrt{0.156^2 + 0.085^2} = 0.178 \text{ cp}$$

This compares with a value of 0.194 cp obtained using the longer method. The Estimated Total Error is $\sqrt{0.162^2 + 0.178^2} = 0.240$ cp which compares quite favorably with the 0.253 cp obtained before. It cannot be identified in advance whether the simplified method will lead to a larger or smaller estimate of the propagated error.

C-5 ADDITIONAL EXAMPLES

Example C-2 Estimating K_{oc} from K_{ow} for 1-chloro-1-bromo-2,2,2-trifluoroethane.

Estimation of the soil adsorption coefficient, K_{oc} , is described in detail in Chapter 4. A variety of empirically-derived regression equations with $\log K_{oc}$ as the dependent variable are given in that chapter. Several of these use $\log K_{ow}$, the logarithm of the octanol-water partition coefficient, as the predictor variable. Thus, the estimating equation is

$$\log K_{oc} = A_1 \log K_{ow} + A_2 \quad (C-21)$$

where A_1 and A_2 depend upon the data set used which may or may not represent a special class of chemicals. Estimation methods for K_{ow} are given in Chapter 1.

To estimate the adsorption coefficient for 1-chloro-1-bromo-2,2,2-trifluoroethane either Eq. 4-7 or 4-8 appears to be appropriate. Equation 4-8 is used for this example and gives:

$$\log \hat{K}_{oc} = 0.544 \log K_{ow} + 1.377 \quad (C-22)$$

Example 1-27 of Chapter 1 demonstrates the estimation of $\log K_{ow}$ for 1-chloro-1-bromo-2,2,2-trifluoroethane. Using the method of fragment constants,

$$\log \hat{K}_{ow} = 2.46 \pm 0.14$$

(The estimate of method error, ± 0.14 log units, was obtained by averaging errors from 76 chemicals with known values.)

From Eq. C-22,

$$\log \hat{K}_{oc} = 0.544 (2.46) + 1.377 = 2.72$$

$$\hat{K}_{oc} = 519$$

Error in \hat{K}_{oc} depends on method error due to using Eq. C-22 and propagated error because of uncertainty in the value of $\log K_{ow}$. Table 4-9 contains information on estimation errors for a number of chemicals. The ratio, Estimated K_{oc} /Measured K_{oc} , varies from 18 to nearly 0 for Eq. 4-8, giving relative errors up to 1700%. The average for those chemicals with K_{oc} between 100 and 1000 is 120%. That value is used for this example.

Estimation of propagated error follows Method 1 in § C-4. The estimation rule is:

$$\hat{K}_{oc} = 10 [0.544 \log (K_{ow}) + 1.377]$$

The single estimated input is $\log \hat{K}_{ow}$. Following the Method 1 steps, we obtain:

$$(1) \hat{C}_1 = 10 [0.544 (2.46 - .14) + 1.377] = 435.6$$

$$(2) \hat{C}_2 = 10 [0.544 (2.46 + .14) + 1.377] = 618.6$$

$$(3) \text{ Propagated Error} = \sqrt{\frac{(435.6 - 618.6)^2}{4}} = 91.5$$

Expressing the method error in K_{oc} units gives:

$$\text{Method Error} = 1.20 (519.1) = 623$$

$$(4) \text{ Total Error} = \sqrt{623^2 + 91.5^2} = 630$$

An alternate (and, perhaps, preferable) approach would be to calculate the total error in terms of $\log K_{oc}$; this avoids having the final range of K_{oc} values include negative numbers. Using this alternate approach, the results of steps 1 to 3 above are 2.64, 2.79, and 0.075, respectively (all in $\log K_{oc}$ units). The method error = $\log 623 = 2.79$ and the total error (from step 4) is also 2.79, again in $\log K_{oc}$ units. For this example, where the input value is estimated quite precisely, total error is almost all due to method error.

Example C-3 Estimating P_{vp} for aniline from ΔH_{vb} and T_b .

Assessing error in the estimated vapor pressure of aniline is the next example. The estimation rule (from Eq. 14-20) is:

$$\hat{P}_{vp} = 760 \exp \left\{ \frac{\Delta H_{vb}}{\Delta Z_b R T_b} \left[1 - \frac{(3-2T_{rb})^m}{T_{rb}} - 2m(3-2T_{rb})^{m-1} \ln T_{rb} \right] \right\} \quad (C-23)$$

where

\hat{P}_{vp} = estimated vapor pressure (mm Hg)

ΔH_{vb} = heat of vaporization at the normal boiling point (cal/mol)

T_b = normal boiling point (K)

T = temperature (K)

$T_{rb} = T/T_b$

m, R and ΔZ_b are constants

The constants $R = 1.987$, $\Delta Z_b = 0.97$, and $m = 0.19$ are considered error-free. However ΔH_{vb} and T_b must be estimated if measured values are not available. Note that $T_{rb} = T/T_b$, where T is the temperature for which the vapor pressure is desired.

Chapter 12 gives methods for estimating T_b . For aniline, the Lydersen, Forman, Thodos method gives $\hat{T}_b = 441.5K$ with an average method error of $\pm 6.8\%$, or $\pm 30K$ for aniline. The heat of vaporization of aniline can be estimated using methods from Chapter 13 as 11,090 cal/mole with an average method error of $\pm 2\%$ (± 222 cal/mole for aniline). The vapor pressure for aniline will be estimated for $T = 20^\circ C$ (293K).

In this setting, estimated vapor pressure depends on two estimated input values, \hat{T}_b and $\Delta \hat{H}_{vb}$. Methods 2 and 3 in §C-4 are applicable here. For completeness, both the full method and simplified method will be used. To set the notation, let

$$\hat{P}_{vp} = f(T_b, \Delta H_{vb}) \quad (C-24)$$

where $f(\cdot, \cdot)$ is the right-hand side of Eq. C-23. The estimate of P_{vp} is

$$\hat{C} = \hat{P}_{vp} = f(\hat{T}_b, \Delta \hat{H}_{vb}) \quad (C-25)$$

$$\begin{aligned} \hat{P}_{vp} &= 760 \exp \left\{ \frac{11,090}{(0.97)(1.987)(441.5)} \left[1 - \frac{(3-2(293)/441.5)^{0.19}}{293/441.5} \right. \right. \\ &\quad \left. \left. - 2(0.19)(3-2(293)/441.5)^{0.19-1} \ln \left(\frac{293}{441.5} \right) \right] \right\} \\ &= 0.52 \text{ mm Hg} \end{aligned}$$

Using Method 2

To assess propagated error with the full method, one must calculate \hat{C}_{11} , \hat{C}_{12} , \hat{C}_{21} , and \hat{C}_{22} .

$$\hat{C}_{11} = f(441.5 - 30, 11,090) = 1.58 \text{ mm Hg}$$

$$\hat{C}_{12} = f(441.5 + 30, 11,090) = 0.20 \text{ mm Hg}$$

$$\hat{C}_{21} = f(441.5, 11,090 - 222) = 0.60 \text{ mm Hg}$$

$$\hat{C}_{22} = f(441.5, 11,090 + 222) = 0.45 \text{ mm Hg}$$

$$\text{Propagated Error for Input 1} = \sqrt{\frac{(1.58 - 0.20)^2}{4}} = 0.69 \text{ mm Hg}$$

$$\text{Propagated Error for Input 2} = \sqrt{\frac{(0.60 - 0.45)^2}{4}} = 0.075 \text{ mm Hg}$$

$$\text{Propagated Error} = \sqrt{0.69^2 + 0.075^2} = 0.694 \text{ mm Hg}$$

Table 14-1 shows that method error for this P_{vp} range is approximately 28% or 0.146 mm Hg. Thus,

$$\text{Total Error} = \sqrt{0.146^2 + 0.694^2} = 0.71 \text{ mm Hg}$$

Using Method 3

This method of estimating propagated error depends only on the values \hat{C}_{11} and \hat{C}_{21} which are calculated by setting \hat{T}_b and $\Delta \hat{H}_{vb}$ respectively at one standard error below their estimated values.

$$\text{Propagated Error for Input 1} = |\hat{C}_{11} - \hat{C}| = |1.58 - 0.52| = 1.06 \text{ mm Hg}$$

$$\text{Propagated Error for Input 2} = |\hat{C}_{21} - \hat{C}| = |0.60 - 0.52| = 0.08 \text{ mm Hg}$$

$$\text{Propagated Error} = \sqrt{1.06^2 + 0.08^2} = 1.06 \text{ mm Hg}$$

$$\text{Total Error} = \sqrt{0.146^2 + 1.06^2} = 1.07 \text{ mm Hg}$$

Estimated total error from the simplified method is not qualitatively different from the estimate obtained using the full method (0.71 mm Hg). As in Example C-2, the ranges associated with the estimated errors imply (wrongly) the possibility of negative numbers. Thus an alternate approach of calculating the propagated and total error in $\ln P_{vp}$ might be preferable.

C-6 SYMBOLS USED¹

- A_1, A_2 = parameters in Eq. C-21
- B_4 = parameter in Eqs. C-1, -2
- C = surrogate symbol for any dependent variable, Eq. C-6

1. A " ^ " above any symbol indicates the value is estimated.

C_1	=	value of C obtained from $f(x_o - s_{x_o})$. See § C-4, Method 1.
C_2	=	value of C obtained from $f(x_o + s_{x_o})$. See § C-4, Method 1.
C_{11}	=	value of C obtained from $f(x_1 - s_{x_1}, x_2, \dots, x_p)$. See § C-4, Method 2.
C_{12}	=	value of C obtained from $f(x_1 + s_{x_1}, x_2, \dots, x_p)$. See § C-4, Method 2.
C_{i1}, C_{i2}	=	values of C when the i^{th} input variable is $x_i - s_{x_i}$ and $x_i + s_{x_i}$, respectively. See § C-4, Method 2.
$f(\cdot)$	=	rule, or equation(s), linking the input variable(s) to the dependent variable, C. See Eq. C-6.
$[df/dX]_{x_o}$	=	first derivative of $f(\cdot)$ evaluated at $X = x_o$, Eq. C-10.
ΔH_v	=	heat of vaporization, Eqs. C-2, -3 (cal/mol)
ΔH_{vb}	=	heat of vaporization at the normal boiling point, Eq. C-23 (cal/mol)
K_F	=	parameter in Eq. C-3
K_{oc}	=	soil (or sediment) adsorption coefficient based upon organic carbon content, Eq. C-21
K_{ow}	=	octanol/water partition coefficient, Eq. C-21
m	=	parameter in Eq. C-23
n	=	parameter in Eq. C-2
p	=	number of input variables (subject to error) in $f(\cdot)$
P_{vp}	=	vapor pressure, Eq. C-23 (mm Hg)
R	=	gas constant, Eqs. C-3, -23 ($= 1.987$)
s	=	estimated standard error
s_{x_o}	=	estimated standard error for the estimated input pa- rameter X_o
T	=	temperature (K)
T_b	=	normal boiling point, Eqs. C-1, -3, -23 (K)
T_{rb}	=	T/T_b , Eq. C-23
X	=	surrogate symbol for any input variable in $f(\cdot)$
X_o	=	true value of X for some chemical
\hat{x}_o	=	estimated value of X_o
X_i, \hat{x}_i	=	true and estimated values for the i^{th} input variable in $f(\cdot)$
ΔZ_b	=	parameter in Eq. C-23

Greek

η_L	=	liquid viscosity, Eq. C-1 (cp)
η_{Lb}	=	liquid viscosity at the normal boiling point, Eq. C-1 (cp)

C-7 REFERENCE

1. Ku, H.H., "Notes on the Use of Propagation of Error Formulas," *J. Res. Nat. Bur. Stand.*, Section C, 70, 263-73 (1966).

D

RECOMMENDATIONS FOR FUTURE RESEARCH AND DEVELOPMENT

D-1 OVERVIEW

All the chapters in this handbook¹ — excluding Rate of Aqueous Photolysis (Chapter 8) and Rate of Biodegradation (Chapter 9) — concern properties for which estimation methods are currently available in previously published works. The estimation methods provided in this handbook were largely selected from these “available methods.” In a few cases the authors of the various chapters were able to offer some new or modified approaches, but they did not develop any totally new methods.

It is expected that future editions of this handbook can be significantly improved over this initial version for two basic reasons:

- (1) New estimation methods and/or property correlations are continually being developed. Relatively few publications appearing after 1979 could be incorporated in this work.
- (2) Project limitations did not allow as detailed an evaluation of available methods as would have been desirable. Many questions remain concerning method errors and extent of applicability to different chemical classes and to a wide range of values.

1. The selection process is described in the Introduction.

Section D-2 below outlines specific areas where future research and development appears to be needed for each of the 26 properties or parameters included in this handbook. In most cases a few basic elements (not always specified) should be included:

- A review of the literature from 1979 on, plus additional contacts with researchers active in the subject areas.
- A compilation, with some focus on the properties of key environmental concern (e.g., Chapters 1-9 or 1-17), and critical evaluation of measured values of the property. Improved estimation methods, especially those based on simple linear regressions, could then be easily obtained for many properties.
- A more analytical evaluation and comparison of all available methods.
- A more extensive evaluation of method applicability to various chemical classes and over the range of possible values.
- A more extensive evaluation of method errors for various chemical classes and ranges of values.
- Method extension to additional chemical classes.
- Development and/or evaluation of methods to predict the effect of environmental variables (e.g., temperature, pH, dissolved salts and organic matter) on important properties and rate constants.

The discussions in §D-2 follow the order used for Chapters 1-26. References to named methods may be found in those chapters.

Section D-3 lists properties not covered in this handbook for which estimation methods are desired.

D-2 PROPERTIES IN THIS HANDBOOK

Octanol/Water Partition Coefficient

(1) The fragment constant method of Hansch and Leo (described in §1-3 of Chapter 1) is continually being improved and expanded by the originators, who remain active in this field. The method description should therefore be updated at an appropriate time to include the latest fragment constant values.

(2) Hansch and Leo have also developed a fragment constant method for ions that is not included in Chapter 1. This method should be evaluated and included in future editions.

(3) A rigorous comparison of the fragment constant method of Hansch and Leo and that of Nys and Rekker has not, to our knowledge, been made. Such a comparison may indicate that both methods may be worth including in future editions and/or that certain features of one method could be incorporated into the other.

(4) The estimation method based upon the use of estimated activity coefficients (obtained via the methods described in Chapter 11) was described only in general terms in Chapter 1. The method was not evaluated, nor were basic steps, method error or examples provided. This method should be explored, since it provides a second route to K_{ow} (using only structural information), is likely to have a relatively low method error, and will allow K_{ow} to be estimated at different temperatures. To develop this method it will be necessary to expand the methods for estimating activity coefficients to the ternary system of octanol (primary component)/water/chemical. Such methods have been described in the literature, and their expansion should not involve a substantial amount of effort.

(5) The method based upon the use of solvent regression equations is currently limited to a relatively small number of solvent/water systems and — for some cases — to a relatively small number of chemical classes. Further search of the literature would probably provide sufficient data for a significant expansion of this method.

Solubility in Water

(1) A significant amount of work is needed to improve the estimation of solubility from octanol/water partition coefficients. This would include:

- Using the best available data to obtain additional regression equations for specific chemical classes. The data sets should include only liquids, and all values should be for the same temperature (e.g., 25°C).
- Using the same data to obtain new equations for mixed chemical classes. Again, the data set should be limited to liquids and to values at a common temperature.

- The solubility correction factor recommended for solids $[-0.0095(t_m - 25)]$ should be further investigated. It may be possible to recommend slightly different, more accurate correction factors for different classes of chemicals.
- The suggestion that better correlations would be obtained if data sets were limited to chemicals with similar values of $\log(K_{ow}S)$ should be investigated. (See "Basis for Method" in Ch. 2.)
- Method errors associated with the existing and/or newly developed regression equations need to be further investigated.

(2) The method of Irmann, which uses atomic and structural fragment constants, should be expanded to include additional atoms and functional groups not presently covered ($-S-$, $>N-$, $-OH$, $=O$, $-O-$, P , etc.).

(3) The use of the connectivity parameter (pathways 13 and 4 in Figure 2-1 of Ch. 2) for the estimation of solubility probably warrants further investigation. It would supply a second method that required only structural information. This method was not recommended in Chapter 2.

(4) The use of estimated activity coefficients for the estimation of aqueous solubility requires further investigation. The range of applicability and accuracy of the method is not well documented. The method is important, since it allows estimation at any temperature and may be more accurate than other methods.

(5) Additional research is needed to further clarify the influence of dissolved inorganics, dissolved organics, temperature, and pH on the solubility of organic chemicals in natural waters and waste waters. Simple equations with correction factors may be possible for some of these parameters.

Solubility in Various Solvents

(1) The general approach selected (i.e., via estimated activity coefficients) has not been adequately evaluated with regard to range of applicability and method errors, primarily because of time constraints. The limits of applicability to different solute and solvent classes must be more closely tied in with the limitations of Chapter 11 (Activity Coefficients). The recommended procedures should be used to estimate

solubilities for a much larger example set, and the results should be compared with measured values so that the method error (with and without the use of estimated activity coefficients) is better defined.

(2) A method for estimating the solubility of gaseous solutes should be selected and included in subsequent revisions.

(3) The general method should be extended to ternary systems and the applicability to liquid-liquid extraction problems explained.

(4) The general method would be significantly simplified if additional regression equations were developed between γ^∞ and some other common property for specific chemical classes.

Adsorption Coefficient for Soils and Sediments

(1) All measured values of K_{oc} for organic chemicals should be compiled. Existing compilations have been limited primarily to pesticides and, to a lesser extent, polynuclear aromatic hydrocarbons; new data on other chemicals are much needed. In its review of values reported in primary publications, the compilation should list mean values, coefficients of variation, and other pertinent statistical information.

(2) With the improved data set described above, new regression equations should be derived not only for the complete data set but also for each chemical class that is adequately represented.

(3) Additional study should be given to the values of n derived from the Freundlich equation. Even if an estimation method for n cannot be derived, it may be possible to give some guidance on the selection of a value for n when calculations of x/m are required.

(4) Estimation methods based upon a correlation between K_{oc} and R_f values (the latter from soil thin-layer chromatography tests) could be developed from data already in the literature. This approach could then be evaluated and compared with methods that are based on the use of data for K_{ow} and S .

(5) Estimation methods based upon a correlation between K_{oc} values and adsorption coefficients for adsorption on activated carbon should be investigated. Numerous studies, including the determination of adsorption isotherms, have been conducted in recent years with activated carbon in conjunction with water and wastewater treatment studies. It is

possible that better correlations may be found than those with K_{ow} or S ; in addition, values of n (obtained by fitting the Freundlich equation to the data) may be similar.

(6) The extension of methods for estimating K_{oc} for soils and sediments to suspended particulate matter should be investigated. Particular attention should be paid to suspended particulate matter in ponds, lakes, and oceans, where microorganisms are numerous.

Bioconcentration Factor in Aquatic Organisms

(1) *Prescreening of Untested Organic Compounds for Bioconcentration Potential*

- Estimated bioconcentration factors are highly useful in prescreening untested organic compounds. Therefore, the range of BCF applicability to aquatic organisms should be further assessed. Specifically, we should determine whether existing estimation techniques can be applied to a broad variety of aquatic organisms with the same order-of-magnitude level of confidence, or whether additional correlations based on phylogenetic differences should be developed. For example, sufficient laboratory bioconcentration data, under bioassay conditions similar to those already developed for freshwater fish, should be developed and compiled for marine and estuarine fish, several phyla of aquatic invertebrates, and aquatic algae/macrophytes. Such data should be used to assess existing or new correlations of bioconcentration with physical/chemical properties of organic compounds such as K_{ow} or S .
- There is some evidence [1] that even where the parent compound does not accumulate to any great extent, metabolites may accumulate, particularly after long-term exposure. Quantifying the relationships between BCFs for parent compounds and their metabolites, particularly for compounds (or classes of active groups) that have low BCFs, would improve the understanding and usefulness of methods to estimate BCF from physical/chemical properties. It would also make BCF estimates more useful for extrapolations of the kind discussed below.

(2) Predictive Models and Extrapolation to Field Situations

- When BCF estimates are to be utilized in model simulations, especially for predictive purposes, additional study should be made of the numerous environmental parameters that could affect bioconcentration, because that might necessitate redefinition of the assumption that an order-of-magnitude level of confidence can be associated with the estimates. In addition to the data described above, information is needed concerning the importance of factors such as size, weight, and lipid content of test organisms and the significance of such environmental parameters as water pH, temperature, and oxygen content relative to bioconcentration and/or metabolism.
- For extrapolation of estimates to field situations, field data must be collected to establish the usefulness and appropriate limitations of estimates of bioconcentration potential. Synoptic data on concentrations in media (i.e., water, sediments) and biota are required; these can be used to calibrate and validate estimation techniques and simulation models.

Rate of Hydrolysis

The state of the art of estimating rate constants for hydrolysis in the aquatic environment is clearly limited by the inadequacy of the existing data base. There are numerous opportunities for further useful research and development; the following are representative suggestions:

(1) Several categories of compounds — amides, nitriles, and esters of sulfonic and sulfuric acids — are potentially hydrolyzable, but no relevant data appear to exist. Studies to determine the range of k_T , k_H , k_O , and k_{OH} for these categories would be worthwhile.

(2) Experimental procedures for additions to the hydrolysis rate constant data base should use pure water if possible or highly aqueous solvent media, cover the range of pH values over which H^+ and OH^- catalysis may be important, and include measurements at three or more temperatures over a range of at least $40^\circ C$ for determination of the temperature dependence. Values of ΔH^\ddagger and ΔS^\ddagger should be reported as indicators of the reaction mechanism.

(3) Many organic compounds of interest are insufficiently soluble to allow determination of their hydrolysis rate constants in pure water

solution. Research is needed to determine what percentage of organic solvent can be added to increase solubility without significantly affecting k and ρ values. It would be very useful to establish whether k 's measured or calculated for 5% or 10% organic-aqueous medium can be extrapolated to natural water conditions.

(4) For each compound category of major concern (carbamate and phosphate pesticides, for example), it would be useful to confirm, via ΔH^\ddagger and ΔS^\ddagger values, the range of substituent changes over which the hydrolysis reaction mechanism is constant.

(5) It would also be useful to develop consistent sets of correlations for k_H , k_O and/or k_{OH} for compound classes where catalyzed hydrolysis is likely to be important. This would allow estimation of k_T and of overall hydrolysis half-lives.

Acid Dissociation Constant

It is not obvious what research and development approaches would be promising or productive in this area. However, present estimation methods for aliphatic acids are clearly less satisfactory than those for aromatic acids, so any future efforts should probably be directed primarily toward the aliphatics.

(1) Taft substituent constants are defined for group R in RCH_2 (e.g., RCH_2COOH , $RCH_2NH_3^+$). It would be useful to develop the data base to see whether correlations could be extended to longer carbon systems, such as $—CH—COOH$.



(2) For aromatic acids, ortho σ -values are not tabulated. It might be useful to expand the data base of ortho-substituted parent acids.

Rate of Aqueous Photolysis

(1) Long-term research directed toward potential development and application of structure-reactivity relationships to photochemical reaction rates might eventually lead to some useful quantitative correlations. In view of the approaches used for modeling photochemical reactivity in the environment (e.g., the work of Zepp *et al.*), it would seem appropriate to explore relationships between structure and quantum yields, ϕ , rather

than between structure and rate constant, k_p . It is not clear what chemical structural features are likely to serve as useful predictors of ϕ , even within a restricted series of compounds. If ϕ were predictable, the value of k_p could then be estimated from the product of ϕ and the overlap between the irradiation spectrum and the spectrum of the chemical, according to current models.

(2) Experimental verification of the independence of ϕ and the wavelength of irradiation within the solar radiation regime would be valuable. A comparison of ϕ_{254} , ϕ_{300} and ϕ_{solar} for several chemicals in dilute aqueous solutions might be appropriate. The test set should include species with $\lambda_{max} > 290$ nm and also species which have $\lambda_{max} < 290$ nm and a long absorption tail into the solar region. If possible, quantum yields should be determined for both overall disappearance and formation of specific degradation product(s).

(3) It would be interesting to determine whether, or under what circumstances, light of > 350 nm ever leads to net chemical reaction of organics.

(4) The data base of molar absorptivities (ϵ) vs wavelength in the solar irradiation region (for use in Zepp-type models) should be expanded.

Rate of Biodegradation

The phenomenon of biodegradation is not yet well understood, and the development of estimation techniques for the process is still far off. Certain steps, however, would at least enable investigators to look for correlations or relationships between the biodegradability of organic compounds and other properties. These steps include:

- (1) Measurement of the biodegradation of a large number of compounds using standardized laboratory tests (e.g., river die-away, soil perfusion);
- (2) Quantification of the rate of biodegradation and derivation of rate constants; and
- (3) Calculation of rate constants for the already existing data base of biodegradation rates (for experiments conducted under standardized conditions and known reaction rate orders).

The initial focus should be on groups of related chemicals. Once a large data base is developed, relationships between biodegradation and other properties, such as solubility or hydrolysis, can be carefully examined.

Atmospheric Residence Time

(1) New and better data should be used to estimate τ by each applicable method given in this handbook, in order to obtain more information on the strengths and weaknesses (or limitations) of each method. Particular attention should be given to the limitations of Junge's correlation.

(2) Additional nonequilibrium models should be developed for cases where the rate of emission to the atmosphere is nonexponential. Solution of the resulting equations should be possible without a computer.

(3) Available atmospheric models that require the use of a computer to calculate τ should be compiled and described in a manner that facilitates use by others. Detailed equations and computer programs for a number of such models have not, to our knowledge, been published.

(4) Methods should be developed for estimating important atmospheric reaction rate constants of organic chemicals (e.g., k_{OH} , k_{O_3}).

(5) Data should be compiled to assess the relative importance of all the major atmospheric reactions that can degrade organic chemicals (e.g., direct and sensitized photolysis, reaction with $OH\cdot$ or O_3). This would help significantly in the estimation of τ via the use of reactivity data.

(6) Better estimates of τ would be possible if more accurate (global) measurements of emissions and ambient concentrations were available. Such data should be obtained for all chemicals with a potential for long atmospheric residence times. A mechanism to keep estimates of atmospheric emissions up to date (e.g., by allowing changes in production rates and pollution control to be factored in) should be developed.

Activity Coefficients

Future studies should concentrate on extending the Pierotti correlations for infinite dilution activity coefficients. These correlations should

be extended to include, at the very least, the interactions of most organic chemicals with water. It seems reasonable to suppose that correlations involving group contributions or fragment constants could be incorporated in a manner that would permit estimation of the constants in the Pierotti equations.

UNIFAC, an elegant and reasonably accurate group contribution method, is continuously being updated. However, as it is mathematically complex and quite tedious to apply, we feel that extending the simpler correlations would be more useful.

Boiling Point

(1) The estimation methods for boiling point assume that compounds are in their normal valence state. This precludes the estimation of compounds containing $-\text{NO}_2$, $-\text{SO}_4$, or $-\text{PO}_4$ groups. Correlations of data for sets of compounds containing these groups should be made.

(2) Tables of parachor and molar refraction structural increments should be updated to include more recent evaluations. The terms used for Meissner's method have not been updated in the past 30 years, although several groups have been active in evaluating parachor and molar refraction.

(3) Evaluation of the computer-based structural correlations, such as molecular connectivity, should be made and transportable computer programs published.

(4) All of the correlations for boiling point are based on single-substituent effects. The effects of multiple substituents should be examined to determine the most appropriate estimation method for such compounds.

Heat of Vaporization

(1) Present methods for estimating heats of vaporization deal primarily with elements in their normal valence state. Compounds containing groups such as $-\text{NO}_2$, $-\text{SO}_4$, $-\text{PO}_4$, and $-\text{NHOH}$ are frequently not estimable. Further work to obtain increments appropriate to these groups should be undertaken.

(2) With methods such as molecular connectivity, heats of vaporization are best calculated by computer. These computer-based methods

should be evaluated and, if warranted, transportable computer programs should be developed.

(3) A comprehensive compilation of heats of vaporization should be made. Only those values obtained by direct measurement should be included; values obtained by condensation methods should be excluded. The tabulation should also include heats of vaporization at several temperatures, if available.

Vapor Pressure

(1) Further research is required in estimating the vapor pressure of solids. The vapor pressure of liquids can be estimated quite accurately with, for example, the Antoine equation. However, this and most other vapor pressure equations fail when applied to solid materials. Method 2 of Chapter 14 is a first attempt at addressing this problem, but considerably more research is required to validate the method for all solid organic materials.

(2) Further studies in correlating vapor pressure with other material properties such as solubility or K_{ow} may prove fruitful, particularly for new materials of environmental concern.

Volatilization From Water

(1) Accurate values of the Henry's law constant (H), vapor pressure (P_{vp}), and solubility (S) are needed for many different chemicals. The reported values often differ widely. Values of P_{vp} and S (which may have to be estimated) are required to estimate H . Mackay *et al.* [4] report what appears to be a fairly easy and quick method for determining H . Since H is such a valuable parameter for environmental assessments, this analytical methodology should be carefully evaluated and, if possible, a "standard method" for the measurement of H should be prepared. Values of H for a variety of chemicals should be measured by this method and compared with other reported or estimated values.

(2) The calculation of a volatilization rate constant is basically dependent on a good value for the gas-phase and/or liquid-phase exchange constant(s). These parameters are presently measured primarily by wind tunnel tests, but the results may not adequately represent the wide range of conditions found in environmental situations. Phase exchange data should be obtained that reflect a variety of water-body

characteristics (depth, flow rate or current speed, surface shape, and area), atmospheric conditions (wind speed, stability, humidity, turbulence, etc.), season (winter, summer, frozen, or open), and other factors. Methods for accurately obtaining a long-term average for these values should also be found.

(3) An accurate method must be found for extending experimentally determined volatilization values to compounds of different molecular weights. Currently available data apply to low-molecular-weight compounds such as water or CO_2 , and the proper way to adjust the values for high-molecular-weight compounds is not known. The current procedure is to multiply by the square root of the ratio of molecular weights, a method of doubtful validity.

(4) It would be useful to have accurate values of the reaeration rate coefficient for many different chemicals. SRI International is presently measuring coefficients for some chemicals. The environmental values of the oxygen reaeration rates for many different water bodies under many different conditions are not accurately known.

(5) The presence of other materials in the water such as sorbents, films, and other pollutants affects the volatilization process. Better methods of accounting for these effects should be found.

(6) Experiments should be conducted *in situ* to verify the results of model predictions. Available model verifications were conducted in laboratories under conditions that supposedly simulated environmental conditions, but their correspondence to actual environmental conditions is not well established.

Volatilization From Soil

Users of volatilization models may face situations involving many different environmental conditions. Also, the chemicals may be spilled on, buried in, or mixed with the soil.

To estimate the volatilization rate, models must therefore be able to address different soil properties, chemical properties, the presence or absence of water, sorption, diffusion, soil cover, and water movement. Some studies have been done on how these factors are related to volatilization of pesticides and herbicides in specific instances. However, little is known about many types of chemicals and how the multiplicity of factors affect their volatilization.

More information and understanding of the factors mentioned above are required if adequate methods are to be found for addressing environmental problems in which the presence and volatilization of chemicals in the soil play important roles. The state of modeling of soil volatilization is at a very preliminary level; we can only marginally address specific issues, let alone general problems, as is illustrated by the variance in results of the models presented in Chapter 16.

Diffusion Coefficients in Air and Water

(1) Theoretical formulas should be developed for the apparent diffusion coefficient of molecules absorbed at the solution/solid interface or solution/air interface in saturated groundwater.

(2) The list of atomic and structural diffusion volume increments (Table 17-4) should be extended to include molecules with phosphorus, bromine, fluorine, and iodine atoms. More molecules containing N, Cl and S should be tested so that the reported values are based upon more data points.

(3) Table 17-5 (the Le Bas Method) should be enlarged to include nitro-nitrogen and cyanides, as well as phosphorus compounds.

Flash Points of Pure Substances

(1) The "ideal" or equilibrium flash point of a pure substance is defined as the temperature at which its saturated vapor pressure curve intersects a curve of lower flammable limit (LFL) vs. temperature. It is recommended that a method be developed for estimation of the LFL.

(2) The flash point estimation methods described are pertinent only to pure substances. Estimation methods for mixtures would be a highly valuable addition to the handbook.

(3) It has been demonstrated that existing flash point and boiling point data for pure substances can be utilized to develop simple correlations for homologous series. The inclusion of such correlations for a wide variety of chemical series would be of help to a significant fraction of book users.

Densities of Vapors, Liquids and Solids

(1) Estimation methods that are less dependent on critical properties should be developed. Grain's method should be tested on a greater

number of compounds to ascertain its accuracy and applicability to a wide variety of chemical classes.

(2) The molecular connectivity approach should be developed for application to a more comprehensive set of chemical groupings; it is presently limited to aliphatic alcohols, acids, and hydrocarbons.

(3) More techniques for estimating vapor density should be developed. While the ideal gas law is adequate for pressures and temperatures encountered in the environment, the present estimation techniques for vapor density at other temperatures and pressures are complex and tedious.

(4) Schroeder's method for estimating molar volumes at the boiling point should be expanded to include more atoms, such as phosphorus.

(5) The data base for the recommended method of estimating solid densities should be expanded to eliminate some of the restrictions on compounds for which the method is applicable.

Surface Tension

Additional research is required with respect to estimating the surface tension of hydrogen-bonded liquids. The surface tension of nonpolar and polar aprotic liquids can be estimated with a fair degree of confidence. With hydrogen-bonded liquids, however, fundamental studies of the nature of the molecular forces affecting the tension at the vapor-liquid interface may be in order. At the very least, a study of possible fragment-constant or group contribution schemes for estimating the effect of hydrogen bonding might be useful.

Interfacial Tension with Water

A more detailed investigation of the relationship between interfacial tension and mutual solubility would be of benefit, particularly if a reasonable temperature dependence could be included. Such investigations might yield a relatively simple yet reasonably accurate estimation technique.

Fundamental studies centered around the pioneering work of Good [2] and others might produce a method for estimating interfacial tension from the properties of the pure components. Again, a study of the

relationship between the constant ϕ (see below) and solubility may prove beneficial.

$$\sigma_{ow} = \sigma_o + \sigma_w - 2 \phi \sqrt{\sigma_o \sigma_w}$$

Liquid Viscosity

Fundamental studies of the transport properties of liquids are in order. In particular, models of the liquid state that more closely represent liquids (as opposed to the condensed-gas models) are required. Although such models would increase the complexity of the description of transport properties, they would be very useful.

Another possible line of investigation, which is essentially empirical, would be a study of further structure correlations and/or group contribution schemes.

Heat Capacity

(1) Heat capacities of gases estimated by the method of Rihani and Doraiswamy are usually sufficiently accurate for practical applications, and the method is general enough to encompass most commercial compounds. Some refinements, such as corrections for cis versus trans isomers might be useful, however.

(2) For liquids, the method of Johnson and Huang is of adequate accuracy for field use but is limited by the number of group contributions for which values have been tabulated. An effort to expand its use would be quite worthwhile. It should especially be broadened in its application to a variety of ring compounds, including heterogeneous rings and unsaturated hydrocarbons. The contributions of a wider range of oxygen-, nitrogen-, and sulfur-containing groups should be determined, if possible.

Thermal Conductivity

The combined method of Sato and Riedel for estimation of thermal conductivity is probably already adequate for most "real-time" estimations under emergency conditions. However, inspection of the errors listed in Table 24-3 would suggest that the most frequent and largest errors result from an *underestimation* of thermal conductivity. This might, for instance, result in part from the multiplier 2.64×10^{-3} being too low generally, or from its being incorrect for certain classes of com-

pounds (e.g., anilines). It would be interesting and probably worthwhile to look for opportunities to improve the accuracy of the method without sacrificing its basic simplicity.

Dipole Moment

There is presently no accurate or widely applicable method for calculating the dipole moment of a molecule. The use of this parameter for predicting a chemical's environmental fate and effects in the field should be investigated; if it appears to be promising, research should be directed at establishing an estimation technique based upon molecular structure and substituent contributions.

Index of Refraction

(1) Test Hansch's method of molecular group substituents to aromatic compounds on a larger sample set of chemicals. The error attributed to this method has not yet been evaluated.

(2) Compare the accuracy, ease of use, and applicability of Vogel's two methods for calculating both n_D and R_D by the molecular group additivity method or the bond refraction method. Also, ascertain if the estimation of n_D is more accurate by using the group increments established for n_D , or by estimating R_D as input to the Lorentz-Lorenz equation, along with the density of the compound at the temperature of interest.

(3) Develop values such as those of Hansch for application to aliphatic, heterocyclic, and other non-aromatic parent compounds.

D-3 PROPERTIES NOT COVERED IN THIS HANDBOOK

The Phase I study for this program [3] identified a number of environmentally important properties of organic compounds for which estimation methods were not available. High on this list were rates of aqueous photolysis and rates of biodegradation; recommendations for these two properties were discussed in §D-2. The other important properties or parameters for which estimation methods are desirable are listed below.

Bioconcentration

(1) Rates of (a) uptake and (b) clearance (and metabolism) by aquatic life.

- (2) Bioconcentration factors for terrestrial organisms, both plants and animals.

Adsorption/Soil Transport

- (3) Rates of (a) adsorption and (b) desorption on soils and sediments.
- (4) Adsorption coefficients for adsorption on minerals (e.g., sand and clay) that are low in organic carbon content.
- (5) Adsorption coefficient for desorption process when hysteresis is present.
- (6) The exponential coefficient, n , in the Freundlich (adsorption) isotherm equation.
- (7) Apparent diffusion coefficient in soils.
- (8) Adsorption coefficient for adsorption on (or absorption in) atmospheric particulates and/or aerosols.

Reactivity

- (9) Rate constants for reaction, in the atmosphere, with (a) OH radicals, (b) ozone, and (c) light.
- (10) Rate constants for reaction, in water, with (a) free radicals and (b) other oxidants.
- (11) Reactivity with common materials of construction.

Environmental Transport

- (12) Deposition velocities for use in assessing air-to-ground (and air-to-surface water) transport pathways. Both wet and dry fallout must be considered.
- (13) Mean lifetimes in soil and water compartments.

Others

- (14) Flammability limits in air.
- (15) Melting point.
- (16) Heat of solution.
- (17) Dielectric breakdown voltages.

Specific recommendations for future research on these properties must await a more intensive study (i.e., literature review and consultation with researchers in the fields covered) than was possible in this program. Some work is under way in areas related to many of these properties, and it is likely that estimation methods could be included in the next edition of this handbook. One area of key interest — rates of uptake and clearance by aquatic life (item 1 above) — is discussed in some detail below.

D-4 ESTIMATION METHODS FOR RATES OF UPTAKE AND CLEARANCE OF ORGANIC MOLECULES AND RECOMMENDED R&D

Bioconcentration factors represent the result of uptake and depuration (elimination or clearance) of organic compounds in aquatic organisms. However, uptake and depuration are governed by different rate constants than are bioconcentration factors, and they are believed to be controlled by somewhat different environmental factors or physical chemical properties; thus, they are considered by some to be ultimately more appropriate for simulation models than the resultant bioconcentration factors.

Work on estimation methods for uptake and depuration of organic compounds is currently in the preliminary stages. For this reason, they were not covered in a separate chapter of this handbook. Nonetheless, it is important to note the development of such estimation methods and the research that remains to be done in this early stage of development.

W. Brock Neely has combined his own work on the relationship between K_{ow} and bioconcentration in fish, the bioenergetics of chemical uptake in fish [6,7,8], and the findings of Norstrom *et al.* [9] to propose methods for estimating uptake and elimination rates of fish for organic compounds in water.

Estimating Rates of Uptake and Clearance

(1) Uptake Model

Norstrom *et al.* [9] define uptake in fish by the following:

$$\frac{dC_f}{dt} = \frac{EC_w R_v}{F}$$

where

- C_f = concentration of chemical in fish
- E = efficiency of chemical transfer across gill membrane
- C_w = concentration of chemical in water
- R_v = volume of water flowing across gills per unit of time
- F = weight of fish

Uptake may also be defined by [7]:

$$\frac{dC_f}{dt} = k_1 C_w$$

where k_1 is a rate constant for the uptake of chemicals.

When these two relationships are combined, it can be seen that if values for R_v and E exist or can be estimated, the rate constant (k_1) for uptake of a chemical can also be estimated, as well as the uptake of the chemical.²

The ventilation volumetric rate (R_v) has been shown to be a function of the oxygen concentration in the water, the total energy metabolism of fish, and the efficiency of oxygen transfer across the gill membrane [7]. In estimates of R_v based on such relationships, the following assumptions were made:

- The efficiency with which oxygen is transferred across gills is a constant;
- Metabolic rates are based on data for 5-gram fish, from which linear models for growth/metabolism were derived.

It has been hypothesized that the efficiency transfer coefficient (E), or the efficiency with which a specific chemical moves across the gill membrane, is a partitioning phenomenon. A good correlation has been shown to exist between calculated values for E and $\log K_{ow}$ (octanol-water partition coefficient) for seven organic chemicals [7]. Hence, the resultant regression equation has been proposed by Neely for use in estimating E : [7]

$$E = 0.07 \log K_{ow} - 0.02$$

2. This discussion of methodology is greatly abbreviated. Readers should consult the original publications [6-9].

(2) Clearance Model (Depuration)

The bioconcentration factor for neutral organic molecules can be defined by:

$$BCF = k_1/k_2$$

where

BCF = bioconcentration factor
 k_1 = rate constant for uptake
 k_2 = rate constant for clearance

Estimates and/or measurements of BCF have been made for a broad range of organic molecules. Methods have been described [7] for estimating k_1 . Thus, k_2 can also be estimated.

Research Needs

(1) Whether estimated rate constants for uptake and depuration are used in prescreening new organic molecules or in simulations, the level of confidence and range of applicability that can be attached to such estimates should be established. Recent laboratory bioassays have created a data base for uptake and depuration of a range of organic molecules under flow-through conditions, and it would be possible to establish tentative confidence limits. However, additional test data are needed to confirm the ability of the above-described estimation methods to project uptake and depuration rates for a range of organic compounds under different water temperatures, water oxygen contents, and sizes of fish, within acceptable levels of confidence.

(2) If it appears that uptake and depuration rates cannot be estimated with an acceptable level of confidence (or if a higher level of confidence is desired), individual assumptions that underlie the estimation methods should be further evaluated. For example:

- The efficiency of oxygen transfer across gills is assumed to be constant, but it may vary with such factors as sediment load, temperature, and fish size. An ability to express such variability may have to be developed for organisms of different size, under different conditions.
- The efficiency of chemical transfer across the gill membrane has been correlated to the octanol-water partition coefficient of seven organic molecules. This hypothesis

should be further tested for a broader range of compounds and new regression equations should be developed if necessary.

- Assumptions concerning growth rate/metabolism of fish may require further testing.

(3) As with estimates of bioconcentration based on relatively short-term bioassays, the role of metabolism and the potential for build-up of metabolites in organisms with long-term exposure should be further investigated. An understanding of the extent of such phenomena, at least for certain types of compounds, is needed to assess the validity of rates of uptake, clearance, and BCF that have been estimated from bioassay data.

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